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REACTOR FUEL PROCESSING

A Quarterly Technical Progress Review

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC, by
STEPHEN LAWROSKI and ASSOCIATES, ARGONNE NATIONAL LABORATORY

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TECHNICAL PROGRESS REVIEWS

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REACTOR FUEL PROCESSING

A REVIEW OF RECENT DEVELOPMENTS

Prepared for DIVISION OF TECHNICAL INFORMATION, USAEC,
by STEPHEN LAWROSKI and ASSOCIATES,
ARGONNE NATIONAL LABORATORY

FALL 1965

VOLUME 8

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Foreword

This quarterly review of reactor fuel processing has been prepared at the request of the U. S. Atomic Energy Commission, Division of Technical Information. It is intended to assist those interested in keeping abreast of important developments in this field. In each Review it is planned to cover those particular subjects in which significant new results have been obtained. The Review does not purport to abstract all the literature published on this field during the quarter. Instead it is intended to bring each subject up to date from time to time as circumstances warrant.

Interpretation of results, where given, represents the opinion of the editors of the Review, who are personnel of the Argonne National Laboratory, Chemical Engineering and Idaho Divisions. Those taking part in the preparation of this issue are J. Barghusen, G. Bennett, L. Burris, Jr., P. Fineman, A. A. Jonke, G. Kesser, S. Lawroski, W. J. Mecham, P. A. Nelson, D. Paige, J. Royal, J. Simmons, R. K. Steunenberg, C. E. Stevenson, and R. C. Vogel. The reader is urged to consult the original references for more complete information on the subjects reported and for the interpretation of results by the original authors.

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Section

I

Reactor Fuel Processing

Commercial Aspects of Fuel Processing

Fuel-Processing Plans

Commercial Fuel Processing in New York State

The first shipment of fuel has been received at Ashford, N. Y., for storage and eventual processing in the plant of Nuclear Fuel Services (NFS), Inc.[1] The shipment was made from the Yankee Atomic Electric Co. reactor at Rowe, Mass., shortly after a license for storage had been issued to NFS by the U. S. Atomic Energy Commission (AEC).[2] The NFS plant is nearly complete and is expected to begin processing[1] in January 1966. The plant, which has been described previously,[2,3] has a capacity of 300 tons of irradiated fuel per year. The processing scheme involves a chop–leach dissolution step followed by Purex solvent extraction. Other fuel shipments from Yankee are to be received shortly, and shipments from the Commonwealth Edison Co. Dresden (Illinois) reactor and from the AEC New Production Reactor (Richland, Wash.) are also to be received before the end of the year.[4]

Previous uncertainty as to rail shipments of spent fuel to the NFS plant was settled by contracts between the reactor owners (the utilities) and the Baltimore & Ohio Railroad. The contract included assumption by the utilities of the risk of negligence on the part of the railroads involved.[5]

Other companies with reported plans for fuel processing are Allied Chemical, General Electric, and Isochem. The last-named firm, jointly owned by United States Rubber Company and Martin-Marietta Corp., has undertaken operation of the AEC fission-products separation plant at Richland, Wash.[1]

Facilities for plutonium-fuel preparation and for isotope separation are being sought by the New York State Atomic and Space Development Authority (ASDA) as satellite enterprises for the NFS processing plant, which is located on the site owned by ASDA. The Authority is offering to invest up to $1.5 million (the amount not to exceed one-third) of the capital cost of the two facilities.[6]

New Commercial Development at Hanford

A joint organization set up by the Douglas Aircraft Co., Inc., and the United Nuclear Corporation has been selected by the AEC for operation of the production-reactor and fuel-fabrication complex at Richland, Wash. Plans underway for the new enterprise will serve to further the AEC objective of establishing an industrial–research–education complex at Richland.[7]

AEC Announcements Concerning State Responsibility in Operations Involving Radioactivity and Fissionable Materials

The AEC has announced its proposal to amend its regulations concerning the conditions under which the individual states may license the possession and use of fissionable materials:[8]

> Commission regulations provide that states which have agreements with the Commission transferring part of the AEC's regulatory authority to the states may license quantities of fissionable materials not sufficient to form a critical mass, that is, a quantity insufficient to create a chain reaction.
>
> At present, the computation of the quantity necessary to form a critical mass is based upon the

total quantity which a person is authorized to receive, possess or use in the entire state, even though the quantity at each location may be less than a critical mass.

The Commission now proposes to amend its regulations to provide that the computation of a critical mass, for purposes of determining whether the AEC or the state will license the user, will be based upon the total quantity at a particular plant or other single location of use. Thus, a licensee who possesses more than a critical mass of fissionable material in a state could do so under a state license so long as he does not have a critical mass quantity at any single location at any one time. If he has a critical mass quantity at a single location, he would be licensed by the AEC.

Oregon is the most recent addition to the list of states that have agreements with the AEC for assuming part of the AEC's regulatory authority over the uses of radioactive materials within their respective states. Agreements had previously been concluded with Arkansas, California, Florida, Kansas, Kentucky, Mississippi, North Carolina, New York, and Texas.[9]

A proposed agreement by Tennessee to assume state control over radioactive materials has been published by the AEC for public comment as part of the reviewing procedure in such cases.[10]

Table I-1 ITALIAN PATENTS CONCERNING PREPARATION OR PROCESSING OF REACTOR FUELS[11]

Patent No.	Issuance date	Patent title
662,412	June 27, 1962	Eddy Current Method of Measuring Annular Offset
662,413	May 29, 1962	Dispersion Hardened Uranium Metal
664,090	May 15, 1962	Preparation of Spherical Uranium Dioxide Particles
664,091	May 16, 1962	Method for Producing UO_2 Bodies
664,096	July 11, 1962	Dissolution of Uranium Fuels
664,097	July 6, 1962	Coating Method and Apparatus
664,257	Nov. 30, 1962	Liquid Phase Sintering of Metallic Carbides
664,313	Dec. 4, 1962	Controlled Nuclear Reactor Dispersions and Method of Making
664,346	Sept. 1, 1962	Fluorination of Oxidic Nuclear Fuel
664,347	Sept. 1, 1962	Double-Baked, Self-Channelling Electrode
665,514	June 25, 1962	Separation of Uranium Metal from Oxides and Slag in the Reduction of Uranium Tetrafluoride
665,516	July 3, 1962	Actinide Carbide Product and Method of Making
665,701	May 14, 1963	Insolubilization of Fission Products
665,705	July 25, 1963	Method of Dissolving Plutonium
665,706	July 25, 1963	Plutonium Recovery from Nuclear Fuel
665,723	Oct. 5, 1963	Plutonium Oxide Spheres and Method of Making
665,724	Oct. 10, 1963	Plutonium Recovery from Neutron-Bombarded Uranium Fuel
665,922	Sept. 25, 1963	Preparation of Uranium Monosulfide
665,936	Sept. 28, 1963	Improved High Alumina Body
665,945	Oct. 11, 1963	Cladding of Nuclear Fuel Elements
665,953	Oct. 25, 1963	Paste Reactor
665,963	Nov. 14, 1963	Sintering Ceramic Shapes
665,964	Nov. 15, 1963	Thermally Stable Mixed Oxides Containing Tungsten or Molybdenum
670,930	Mar. 13, 1963	Immiscible Liquids Separator

AEC-Owned Patents Made Available for Licensing

The AEC has announced patents newly available for licensing. They comprise 34 AEC-owned Italian patents[11] and 27 AEC-owned Australian patents.[12] The titles considered relevant to fuel processing are listed in Tables I-1 and I-2. (W. J. Mecham and A. A. Jonke)

Table I-2 AUSTRALIAN PATENTS CONCERNING PREPARATION OR PROCESSING OF REACTOR FUELS[12]

Patent No.	Issuance date	Patent title
229,968	Sept. 24, 1958	Sintering Metal Oxide
233,281	Jan. 9, 1959	Nickel-Base Alloy
233,817	June 9, 1959	Fused Salt Process for Recovery of Values from Used Nuclear Reactor Fuels
235,619	July 21, 1959	Removal of Certain Fission Product Metals from Liquid Bismuth Compositions
235,824	Feb. 25, 1959	Extraction of Uranium
236,602	Aug. 26, 1959	Discharge Valve for Granular Material
238,436	Jan. 6, 1960	Improved Process for the Preparation of Uranium Tetrafluoride from Uranium Dioxide
244,479	Feb. 27, 1961	Flame Denitration and Reduction of Uranium Nitrate to Uranium Dioxide
246,105	Mar. 17, 1961	Improved Stripping of Uranium from Organic Extractants
246,320	Jan. 25, 1961	Vibration Compaction
248,575	Aug. 8, 1961	Preparation of UO_2 for Nuclear Reactor Fuel Pellets
250,145	May 24, 1960	Plutonium Alloys Containing Controlled Amounts of Plutonium Allotropes Obtained by Application of High Pressures
250,909	May 3, 1961	Uranium Extractant for Phosphoric Acid Liquors
252,938	Feb. 27, 1961	Method for Obtaining Plutonium Metal and Alloys of Plutonium from Plutonium Trichloride

References

1. Private Firms Set To Reprocess Nuclear Fuel, *Chem. Eng. News*, 43(26): 26-27 (June 28, 1965).
2. *Reactor Fuel Process.*, 8(1): 5 (Winter 1964–1965).
3. *Reactor Fuel Process.*, 6(4): 1 (Fall 1963).
4. AEC Issues License for Storage of Irradiated Nuclear Fuel at Plant in New York, AEC Press Release H-127, May 28, 1965.
5. *Nucleonics Week*, 6(21): 1-2 (June 3, 1965).
6. *Nucleonics Week*, 6(17): 4 (Apr. 27, 1965).
7. *Nuclear Ind.*, 12(5): 3-6 (May 1965).
8. AEC Proposes Amendment to Regulations on State Licensing of Fissionable Materials, AEC Press Release IN-592, June 5, 1965.
9. AEC Approves Agreement with Oregon, AEC Press Release H-136, June 8, 1965.
10. AEC Publishes Agreement Proposed by Tennessee, AEC Press Release H-131, June 3, 1965.
11. Abstracts of 34 AEC-Owned Italian Patents Made Available for Licensing, AEC Press Release IN-597, June 25, 1965.
12. Abstracts of 27 AEC-Owned Australian Patents Made Available for Licensing, AEC Press Release IN-588, May 19, 1965.

Section

II

Reactor Fuel Processing

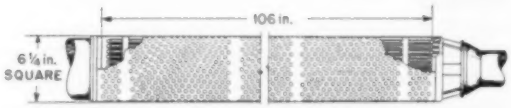
Research and Development on Aqueous Processing

Recent work on U–Pu recovery has been concerned with methods of shearing oxide fuels, processing of BeO-based fuels, and the application of ion exchangers. Considerable work is also being done on the recovery and purification of transuranic elements (neptunium, americium, and curium). Plant equipment and instrumentation have also received attention.

Mechanical Preparation for Fuel Processing

Finney of Oak Ridge National Laboratory (ORNL)[1] describes a mechanical device to remove rows of tubes from the Consolidated Edison Company core B fuel assembly shown in Fig. II-1. After the tubes are removed, it is then possible to shear, using the 250-ton shear as previously described in the Winter 1964–1965 issue of *Reactor Fuel Processing*.[2]

The assembly is clamped in the device shown in Fig. II-2 after the ends are removed by abrasive sawing. The fuel-assembly "eggcrate" is forced against the ejector plate by the



Physical data

Component	Weight, kg
173 S.S. tubes—one spring per tube (0.317 in. in inside diameter by 0.012 in. in wall thickness by 105 in. long)	31.69
Sheath and grid sections	12.45
End adapters	21.85
UO_2 pellets	228.89
Total	~294.74 (648 lb)
Total (excluding end adapters)	~272.89 (600 lb)

Fig. II-1 Westinghouse–Consolidated Edison core B fuel assembly.[1]

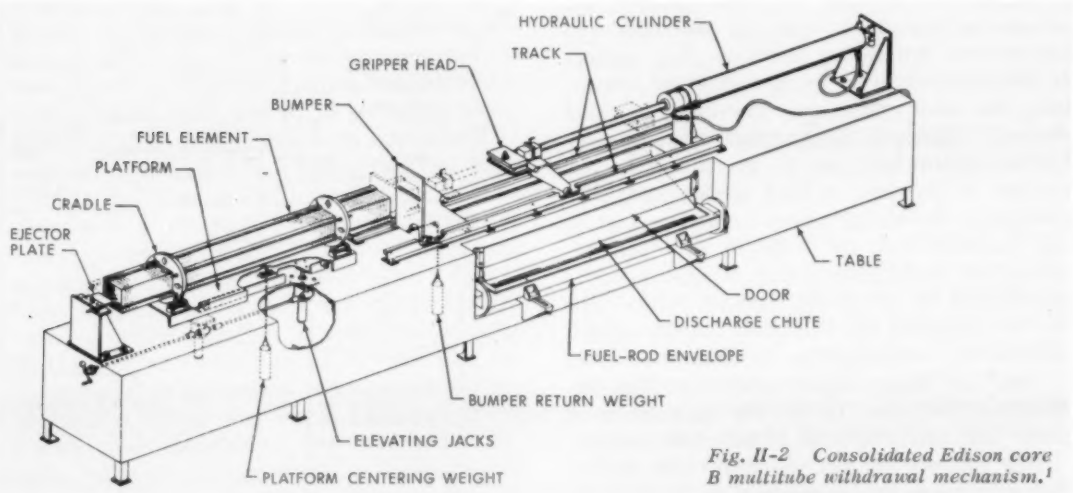


Fig. II-2 Consolidated Edison core B multitube withdrawal mechanism.[1]

bumper and a hydraulic cylinder to displace one row of tubes which are then gripped and pulled from the assembly by another hydraulic cylinder. This procedure is repeated with proper manipulation of the assembly until the assembly is empty of tubes.

Preliminary tests show a required force of 300 to 420 lb to eject and 240 to 315 lb to pull 14 tubes; it is expected that the required force would be somewhat higher for irradiated elements. (D. M. Paige)

Processing BeO-Based Fuels

The use of beryllia (BeO) as a moderator in high-temperature reactors fueled with enriched uranium is of interest because of the possibility of developing a practical thermal breeding power-producing reactor with this system. However, because of the high cost of BeO, the necessary investment in moderator is quite heavy. If the moderator is physically separated from the fuel, no unusual processing problems are expected, but, if BeO is used as a diluent and matrix in ceramic dispersion fuels, as in a reactor system of interest to the Australian Atomic Energy Commission, difficult processing problems are created. The advantage of recovering and reusing the BeO, because of its high value, considerably augments these problems.

Cairns[3] has recently reviewed the need for processing in such a system and has considered appropriate processing methods. The subject of beryllium recovery by acetylacetone extraction has been considered previously in this Journal.[4] The fuel dispersions considered by Cairns contain less than 1% uranium and a few percent of thorium in BeO. If this fuel were completely dissolved, a very-low-concentration fuel solution would be produced as a solvent-extraction feed. Consequently it appears most appropriate to grind the ceramic dispersion and to leach the fuel selectively in nitric acid, followed by centrifugation, in order to prepare a feed for liquid–liquid extraction. The undissolved BeO and the U–Th–Be solution in nitric acid are processed as separate streams.

The undissolved BeO is recovered by the Berox process. This involves dissolving the centrifuge cake in sulfuric acid and converting the beryllium into the oxyacetate by adding an acetate, followed by azeotropic distillation in the presence of propyl acetate to remove water. After crystallization of the oxyacetate, the beryllium is reconverted to the oxide by hydrolysis and calcination. Decontamination from fission products in this process is reported to be good.

The U–Th–Be solution in nitric acid obtained by leaching the ground oxide, which may be as concentrated as 2.5*M* beryllium, is then extracted with tributyl phosphate (TBP) in a hydrocarbon solvent to separate the thorium and uranium from the beryllium. Because of the acidity of the feed solution, the use of a split contactor is proposed to allow extraction of uranium and thorium at low acidity without hazard of separation of a third phase. The flow sheet proposed is given in Fig. II-3. This flow sheet has been tested, using laboratory-scale mixer–settlers and nonirradiated feed solutions, with satisfactory results.

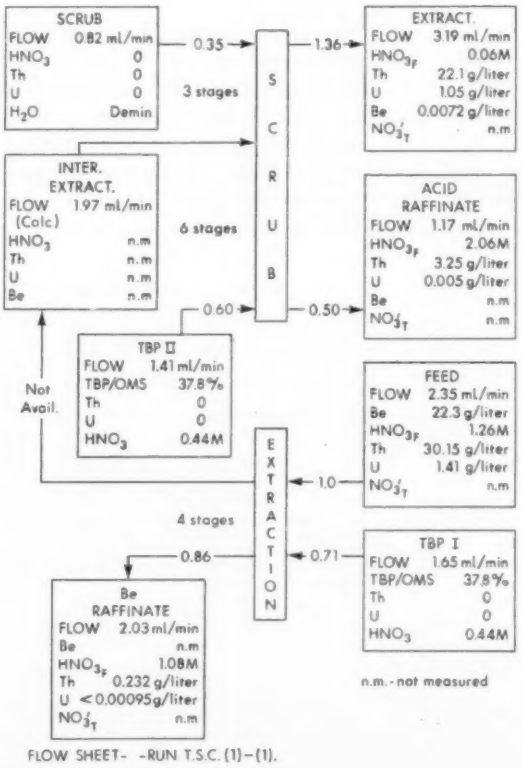


Fig. II-3 Split contactor flow sheet for separation of thorium and uranium from beryllium.[3]

Ion-Exchange Processes

Plutonium Processing

Anion exchange is a well-recognized process for the concentration and purification of plutonium recovered from processing reactor fuels. Plutonium is sorbed as the hexanitratoplutonate ion, $Pu(NO_3)_6^{2-}$, on resins of sulfonated polystyrene type, for example. James has recently reported on continuing studies at Los Alamos on the characteristics and mechanism of this process.

In the first of two reports, James discusses methods of calculating the performance of fixed-bed columns of strong-base anion-exchange resin (Dowex 1-X4) from a strong (7 *M*) nitric acid solution and compares the results of such calculations with experimental data.[5] It was intended to develop a method for predicting the time-dependent concentrations in the fixed bed and the effluent. The appropriately solved partial differential equations could not be used directly because of the slow diffusion rate of plutonium in Dowex 1-X4 and the inconsistency of the diffusion coefficient; the use of a two-step numerical solution was necessary. In batch and column equilibrium experiments, the agreement of observed and calculated values for the concentration of plutonium in the resin phase was such as to indicate the validity of the equations developed.

In a second report by James,[6] the results of studies on plutonium anion exchange are extended to sorption from mixed aluminum nitrate–nitric acid systems, since the aluminum, although not readily sorbed, is frequently introduced in plutonium purification operations. A method is described for calculating the equilibrium distribution coefficients for sorption of plutonium at trace level concentrations on Dowex 1-X4 resin from solutions containing 2.3 *M* to 9.0 *M* HNO_3 and 0.1 *M* to 1.26 *M* $Al(NO_3)_3$, based on parameters which are functions of the molar concentration of nitrate ion, and the mole ratio of hydronium ion to water, in the solutions. The agreement of estimated and experimental values was within 24%. Use of the tracer-level distribution coefficients and kinetic relations previously derived permits development of the equilibrium absorption behavior of Pu(IV) on Dowex 1-X4 from any aluminum nitrate–nitric acid solution.

Zirconium Phosphate Ion Exchangers

Inorganic ion-exchange media are of considerable interest in the field of nuclear processing because of the presumably greater resistance of such media to degradation under irradiation than occurs in the case of organic polymeric media. One type of material of interest in this connection is hydrous zirconium oxide. Cation exchangers prepared from acidic oxides (zirconium phosphate, tungstate, or molybdate) have previously been noted to have remarkable selectivity for the various alkali metals.[7]

Ahrland and Albertsson have recently described equilibrium studies with zirconium phosphate gels having Pu-to-Zr ratios varying from 1.1 to 1.95. Alkali, alkaline-earth, rare-earth, and uranium nitrate or perchlorate solutions provided the cations whose sorption was studied. The ions were largely those occurring as fission products. The distribution-coefficient data quoted are extensive and indicative of the feasibility of effecting useful separations of these ions. For example, when a gel with a Pu-to-Zr ratio of 1.1 is used, U(IV) is strongly sorbed at a *p*H of 0, UO_2^{2+} and Cs^+ are sorbed at *p*H 1.0 to 2.0, and Ce^{3+} is sorbed at *p*H 1.5 to 3.0, whereas for strong sorption of Sr^{2+}, the *p*H must be greater than 3.0. Gels with a Pu-to-Zr ratio greater than 1.5 were found to behave as ideal cation exchangers, whereas those with a lower Pu-to-Zr ratio were found to sorb metal ions without releasing an equivalent amount of H^+. This is evidence of an amphoteric character of gels having low Pu-to-Zr ratios.

Neptunium-Recovery Processes

Since ^{238}Pu is becoming increasingly valuable as a long-lived energy source for space vehicles, interest in methods for the separation of ^{237}Np, from which ^{238}Pu can be prepared by irradiation, has also increased. The separation techniques employed were recently reviewed.[9] In France, trilaurylamine (TLA) has been employed as a solvent for neptunium recovery. In other studies, means for reducing the gas formation in neptunium process solutions, which adversely affects the performance of ion-exchange resins, have been reviewed.

Extraction of Neptunium by Trilaurylamine

In a report from the French Atomic Energy Commission, Champion and Chesne note that TLA, diluted with dodecane, provides a very useful solvent for the recovery, separation, and decontamination of neptunium and plutonium from irradiated fuels, and they illustrate this finding with results of processing material on a semiworks scale at the Marcoule Plant.[10] Their procedures utilize ferrous reduction, nitrite oxidation, and sulfate complexing in a variety of schemes.

In nitrate media the great selectivity of TLA for Np^{4+} is the basis of schemes suitable for the solution of various problems:

1. For the simultaneous extraction of neptunium and plutonium, in which all other elements remain in the aqueous phase, there are two possibilities:
   (*a*) Control of oxidation–reduction potential with the Fe^{3+}/Fe^{2+} system, or
   (*b*) Use of two-zone extraction equipment, in which the first zone contains NO_2^- to favor Pu^{4+} extraction, and the second zone contains Fe^{2+} to favor Np^{4+} extraction.
2. Extraction of neptunium and plutonium separately by
   (*a*) Employing a reducing medium (Fe^{2+}) to extract Np^{4+}, and
   (*b*) Employing an oxidizing medium (NO_2^-) to extract Pu^{4+}.
3. Stripping of the two elements from the solvent
   (*a*) Simultaneously by a mixture of nitric and sulfuric acid, or
   (*b*) Separately by a reducing strip for Pu^{4+}, and, in the absence of plutonium, stripping of Np^{4+} with nitric and sulfuric acid.

For processing of irradiated ^{237}Np after HNO_3 dissolution, it is proposed to extract neptunium and plutonium simultaneously with TLA and to strip the two elements together to provide a first decontamination cycle. The second cycle would then involve simultaneous extraction, followed by separate stripping of plutonium and neptunium. A description is given of a pilot-plant test, in which the feed material consisted of a second-cycle raffinate from the Marcoule Plant and which yielded 22 g of ^{237}Np decontaminated from Zr–Nb by factors of greater than 1000.

Reduction of Gas Formation in Solutions

At Savannah River, neptunium is recovered by anion exchange from the first-cycle aqueous waste and is decontaminated and separated from plutonium by further anion-exchange cycles. A similar process is used for recovering ^{238}Pu from ^{237}Np targets. A widely used procedure for valence adjustment when both neptunium and plutonium are to be adsorbed involves reduction with ferrous sulfamate followed by heating. When a solution so treated is passed through an anion-exchange bed, gas may be formed which accumulates in the bed and causes channeling and disruption. Dukes, Burney, and Wallace[11] have recently reported on the composition of the gas and on methods for its elimination.

The gas was found to be principally nitrogen, resulting from the reaction of residual sulfamate ion with traces of nitrous acid. It was found that gassing could be eliminated by destroying sulfamate with an excess of nitrous acid, followed by vigorous degassing. In a plant test of this procedure, losses of ^{238}Pu were slightly higher than with the normal process, presumably as a result of radiolytic oxidation due to ^{238}Pu alpha activity. Consequently a number of reagents were tested as alternatives to sulfamate in conjunction with ferrous ion. The most satisfactory was a solution of ferrous nitrate stabilized against oxidation by aminoguanidine and hydrazine.

Recovery and Separation of Americium and Curium

Chemical processing operations for the recovery, separation, and decontamination of americium, curium, and heavier elements form an important part of the AEC's transuranic-element production program.[12] Solvent-extraction and ion-exchange techniques are much used in this program. In the extraction process a tertiary amine solvent may be used.

Four recent reports have dealt with various aspects of americium and curium processing. The first of these reports considers the principal impurities found in the amine solvent and their effects on processes. The second report is a survey of organic solvents useful for elution of americium and curium from ion-exchange resins. The third report recounts experiences in the purification of 10 curies of ^{242}Cm, whereas the fourth describes procedures

used in the purification of gram quantities of crude $^{241}AmO_2$.

Impurities in Commercial High-Molecular-Weight Tertiary Amines

The commercial mixture of tertiary octyl and decyl amines known as Alamine 336 (and as Adogen 364), diluted with an aromatic solvent such as diethylbenzene, is used to extract transuranium elements from a concentrated lithium chloride solution in the Tramex process developed at ORNL. In laboratory-scale process tests using this solvent at Savannah River, problems were encountered when stable emulsions were formed, or when voluminous precipitates appeared in the solvent phase. It was felt that these difficulties were caused by impurities in the extractant.

Orebaugh[13] has recently described a study carried out at Savannah River on the nature of impurities found in samples of the tertiary octyl–tertiary decyl amine mixture obtained from two sources. Secondary amines of similar hydrocarbon structure were the principal impurities found, although one of the samples also contained a reducible species that could be removed by charcoal treatment. It was verified that the precipitates which formed when the amines in hydrocarbon solution were placed in contact with slightly acid 11*M* lithium chloride solution consisted mainly of secondary amine hydrochlorides. Considerably larger quantities of precipitates were formed when tests were made with free amines rather than with amine hydrochlorides, and when hexane was used as diluent instead of diethylbenzene. Consequently hexane was used to aid in obtaining sufficient material for examination.

The presence of secondary amines (and smaller amounts of primary amines) is not unanticipated, since manufacturers' specifications permit up to 4% secondary amine and 2% primary amine in the ordinary commercial grades. For use as Tramex solvent, a specification requiring at least 99% tertiary amine, and not over 1% secondary amine, with negligible amounts of alkyl radicals above dodecyl and below hexyl, was suggested. Reducing substances should be absent, and the material, when diluted with diethylbenzene, should pass a test involving contact with acid lithium chloride without the production of a precipitate and with rapid phase separation.

Organic Elutriants for Ion-Exchange Resins

Some time ago, Hines, Wahlgren, and Lawless[14] at Argonne reported that an excellent separation of americium from curium could be obtained by sorption of the two elements on a column of ion-exchange resins, followed by elution with a nitric acid–methanol mixture. Earlier, good separations of the individual light rare-earth elements had been secured by this technique, and it was hoped that it might generally be used for actinide-element separations. Potential advantages are: no need for corrosive or highly salted reagents, room-temperature operability, low cost and ready availability of the elutriant in pure form, and ease of recovery of the products from solution. A disadvantage of using methanol, however, lies in its volatility and fire hazard. This is of particular concern for hot-cell operations with intense alpha emitters.

In view of the interest in this technique, Stewart, Bloomquist, and Faris[15] recently completed a survey of more than 60 water-miscible organic solvents that might be used in place of methanol for this purpose. In the initial phase of this work, distribution coefficients for a broad spectrum of rare earths were obtained by spectrographic means using Dowex 1-X4 resin. This work indicated that ethanol, Cellosolve, and methanol–amyl acetate mixtures are at least as effective as methanol in rare-earth sorption.

In a second phase, 22 possibly useful solvents were selected from a group of 57 solvents tested by determination of the distribution coefficient for Am^{3+} ion in systems consisting of 90% solvent–10% 5*M* nitric acid. Distribution coefficients ranged from 305 to 6065 for the solvents of interest. The group consisted of 10 aliphatic alcohols, ranging from methyl to amyl, and fluoro-alcohols, glycols, glycol ethers, esters, ketones, and acids of similar boiling ranges. In a final part of the study, distribution coefficients and separation factors were determined for 12 of these solvents, using americium, curium, promethium, terbium, and thulium. The following nine solvents were then determined to be the most suitable as alternatives to methanol for these separations:

n-Butyl alcohol	2-Mercaptoethanol	Acetic acid
n-Amyl alcohol	Cellosolve	Propionic acid
3-Methoxybutanol	Carbitol acetate	Tetrahydrofurfuryl acetate

Certain of these solvents were also indicated to be potentially usable for the difficult americium–promethium separation.

Purification of Curium and Americium

Horwitz et al.[16] at Argonne have recently described the separation and purification of 10 curies of ^{242}Cm (obtained by neutron irradiation of 45 mg of $^{241}AmO_2$) by solvent extraction, ion exchange, and precipitation. Following caustic–nitrate dissolution of the aluminum capsule, the oxide was dissolved in 8*M* HCl, and the bulk of the fission products was removed by batch extraction with Alamine 336 in diisopropylbenzene. Americium, curium, and rare-earth fission products were then sorbed together on Dowex 1 resin from 11.5*M* lithium chloride solution to effect a separation from rare earths by elution of the latter with 10*M* lithium chloride. The actinides were then stripped off the resin with 2*M* HCl, purified by hydroxide precipitation, and oxidized with hypochlorite to permit separation of pentavalent americium by carbonate precipitation. The curium, after further purification by carrying on ferric hydroxide, contained 15% americium and was obtained in 93% yield from the americium–curium mixture.

On a related subject, Hagan and Miller have reported work at the Rocky Flats plant on the recovery and purification of americium.[17] Miscellaneous residues (filters, rags, paper, etc.) containing americium were digested with hot concentrated HCl; the solution was filtered and diluted, and the americium was precipitated as the oxalate along with lead, calcium, cerium, potassium, and plutonium. Purification of the calcined oxides was effected by absorption and elution from both cation resin (Dowex 50-X8) and anion resin (Dowex 1-X4) columns, using thiocyanate for complexing and elution. The AmO_2 content of the product was increased by the resin treatment from 42% to 86 to 98%.

(C. E. Stevenson)

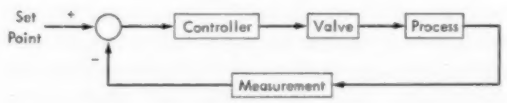
Equipment Design

Compact solvent-extraction equipment continues to be of interest as a means of minimizing radiation damage to solvents used in extraction of irradiated fuels by minimizing contact time. In a recent report from ORNL, Whatley et al. report[18] data on 145 runs using a Mark X stacked-clone contactor reviewed previously[19] (or slight variation). Tables II-1 and II-2 present the conditions and results that were also plotted in the report. The authors state that the most significant result found thus far is the fact that these clones can operate at high aqueous-to-organic ratios (up to 50) without significant organic entrainment. Over fairly wide variations in conditions, efficiencies per stage varied from 31 to 84%.

Process Instrumentation

As a result of a paper presented at the colloquy on Instrumentation in Plants for the Chemical Reprocessing of Irradiated Fuels, held in Paris on Nov. 22–23, 1963, a report[20] has been prepared by Jobe summarizing the practices in U. S. processing plants.

Jobe builds his discussions around the following closed-loop system:



He then discusses the more important of these blocks with respect to U. S. plants.

The process block is considered the most difficult to describe mathematically because of the complex and interrelated unit operations and the varying modes of operation. The Purex two-cycle process is cited as an example: raffinate recycle is used at Hanford, but not at Savannah River. Also, pulse columns are used at Hanford, whereas mixer–settlers are used at Savannah River.

For the measurement block, Jobe points out that, although much effort has been put on primary variable measurements (chemical composition and radioactivity), most plants have had to depend on utilizing secondary variables such as density, liquid or interface level, flow rate, acidity, pressure, or temperature.

Several measurement instruments are discussed in detail, and Table II-3 gives a very good summary of in-line process instrumentation of the more advanced type making use of primary variables. An extensive bibliography is given in the paper.

The measurement of a secondary variable, such as capacitance, conductivity, and density,

Table II-1 DESCRIPTION OF COMPONENTS IN THE STACKED-CLONE CONTACTOR[18]

Run series	Extraction clones		Polishing clones		Feed ports		Vortex finders			Underflow chamber depth† (extraction section), in.	Underflow gap		No. of extraction clones‡
							Diameter		Extension,* extraction section, in.				
	Type mark	Nominal length, in.	Type mark	Nominal length, in.	Extraction section, in.	Polishing section, in.	Extraction section, in.	Polishing section, in.			Extraction section, in.	Polishing section, in.	
907	X	4.0	XII	2.0	3/16§	3/16	0.5	0.4	3/8	1/4	1/8	1/8	7
912-952	X	4.0	XII	2.0	3/16	3/16	0.5¶	0.4	3/16	1/4	1/16	1/8	7
958-964	X	4.0	XII	2.0	3/16	3/16	0.5¶	0.4	3/16	1/4	1/16	1/16	7
970-976	X	4.0	XII	2.0	3/16	3/16	0.5¶	0.4	3/16	1/4	1/16	1/8	7
2M-6, 12, 17	X	4.0	XII	2.0	3/16	3/16	0.5¶	0.4	3/16	1/4	1/16	1/8	7
2M-22	XIII	2.5	XII	2.0	3/16	3/16	0.5¶	0.4	3/16	1/4	1/16	1/16	5
2M-28	X	2.5	XII	2.0	3/16	3/16	0.5¶	0.4	3/16	1/4	1/16	1/16	5
3M-1A	X	4.0	XII	2.0	3/16	3/16	0.5¶	0.4	3/16	1/4	1/16	1/8	7
3M-1B, 4	X	2.5	XII	2.0	3/16	3/16	0.5¶	0.4	3/16	1/4	1/16	1/16	5
3M-8, 12	X	4.0	XII	2.0	3/16	3/16	0.5¶	0.4	3/16	1/4	1/16	1/16	7
3M-16	X	4.0	VI**	4.0**	3/16	3/16	0.5¶	0.4	3/16	1/4	1/16	1/16	7
3M-20	X††	4.0††	VI**	4.0**	3/16††	3/16	0.5†††	0.4	3/16††	1/4††	1/16	1/16	7‡‡
1M-1	X	4.0	VI**	4.0**	3/16	3/16	0.5¶	0.4	3/16	1/4	1/16	1/16	7
1M-6	XV§§	3.0§§	VI¶¶	4.0¶¶	3/16	3/16	0.5¶	0.4	0	3/4	1/16	1/16	4
1M-28	XVI	4.0	XII***	2.0	3/16	3/16	0.5¶	0.4	0	0	1/16	1/16	7

*Polishing-section vortex finders are simpler orifices and have no extension.

†The underflow chamber does not exist in the polishing stages.

‡Four polishing clones in every run.

§Clones 2 and 3 had a 1/4-in. feed port.

¶Clone 1 vortex finder diameter is 0.45 in.

**Clone 11 is a Mark XII 2-in. clone.

††Clone 1 is a special small-bore (3/16- by 1/2-in. taper) 2.5-in.-long clone having a 0.09-in. feed port, a 3/16-in.-diameter vortex finder with no extension, and a 0.5-in. underflow chamber depth.

‡‡Includes special top clone (see footnote ††) that was assumed to have no contribution to the mass-transfer efficiency; efficiency calculations were based on six clones.

§§Clone 4 is a Mark X 3 1/2-in. clone.

¶¶Clone 8 is a Mark XII 2-in. clone.

***Stainless-steel polishing clones.

Table II-2 PERFORMANCE DATA FOR STACKED-CLONE CONTACTOR[18]

Run series	Aqueous phase $NaNO_3$, M	Organic phase % TBP in Amsco	Temp., °C	K_0	Compromise K_0	Average flow ratio (A/O)	Throughput at flooding, cm^3/min	Average extraction efficiency, %	Average stripping efficiency, %	Average efficiency at compromise K_0, %	Performance factor	Rms deviation from average efficiency
907	1	18.5	40	3.32	3.27	3.78	3160	72.2	88.7	84.3	2.66	23.8
912	1	18.5	40	3.05	3.15	3.08	3620	80.0	59.1	65.4	2.37	5.0
919	1	18.5	40	3.28	3.00	4.01	3960	33.8	80.6	63.3	2.51	6.7
925	1	18.5	40	4.33	4.48	3.69	3750	77.3	63.5	71.1	2.67	2.5
931	1	18.5	40	4.34	4.08	3.07	3380	61.0	81.5	66.2	2.24	4.1
937	1	18.5	40	3.57	3.52	3.06	3410	52.2	56.1	53.6	1.83	10.1
946	1	18.5	35	4.45	4.44	3.53	2720	57.0	58.3	57.4	1.56	4.5
952	1	18.5	30	5.44	4.92	3.29	2100	45.7	85.6	52.3	1.10	3.7
958	1	18.5	40	3.92	3.80	3.19	3140	60.9	71.6	64.3	2.02	4.8
964	1	18.5	40	3.86	3.78	3.23	3150	63.1	69.5	65.3	2.06	3.7
970	1	18.5	45	3.27	3.03	3.10	3790	64.0	97.1	75.0	2.84	3.2
976	1	18.5	48	2.97	2.79	2.95	4220	68.1	96.7	79.4	3.35	2.6
2M-6	2	18.5	40	15.6	15.3	15.0	5890	56.0	63.4	60.2	3.55	7.2
2M-12	2	18.5	45	14.4	14.5	15.1	6090	113.0	73.1	75.1	4.57	22.8
2M-17	2	18.5	50	13.6	13.2	12.9	6140	59.0	74.0	66.7	4.10	4.4
2M-22	2	18.5	40	17.3	17.0	12.8	6490	30.1	33.1	31.3	2.03	3.4
2M-28	2	18.5	40	16.4	16.8	13.9	5010	45.3	39.1	42.6	2.13	5.6
3M-1A	3	18.5	45	46.0		12.7	6190	50.9	12.3			
3M-1B	3	18.5	40	41.8	44.0	42.5	6280	47.7	30.4	40.4	2.54	5.1
3M-4	3	18.5	40	56.2	57.3	44.5	6280	37.1	32.5	35.4	2.22	4.1
3M-8	3	18.5	40	45.8	51.1	44.7	6290	385.0	46.3	81.5	5.13	31.4
3M-12	3	18.5	40	49.3	49.4	49.7	6300	46.6	45.7	45.9	2.89	15.5
3M-16	3	18.5	40	47.1	52.7	35.8	5960	51.1	27.7	40.6	2.42	3.4
3M-20	3	18.5	41	52.5	47.2	34.5	6670	42.5	62.2	48.3	3.22	3.5
1M-1	1	18.5	41	2.27	2.78	3.71	3580	483.0	48.9	76.6	2.74	8.9
1M-6	1	18.5	41	3.62	3.46	3.56	3550	49.6	62.9	55.3	1.96	3.8
1M-28	1	18.5	40	4.18	4.10	3.06	3950	46.7	53.0	48.2	1.90	4.2

Table II-3 SUMMARY OF IN-LINE PROCESS INSTRUMENTATION[20]

Instrument and principle of operation	Variables determined	Reliability	State of development	Accuracy	Range of instruments used
Alpha Monitor: Counts pulses from phototube activated by visible light from interaction of alpha particles with zinc sulfide phosphor in direct contact with solutions.	Total alpha activity from various emitters: Pu concentrations at medium range (in aqueous solutions). Traces of alpha activity in waste streams. High levels of alpha activity in process solutions. Low level for bioassays. High level for process streams.	Good; system is simple; suitable for in-canyon installation	Number of units in operation; no sampling; work needed on organic streams and better phosphors.	±20%	0.05 to 10 g of Pu/liter; detection limit of 0.01 g/liter 3.3×10^{-4} μc/ml 5×10^{3} to 1.5×10^{8} dis/(min)(ml)
The solid-state silicon-wafer type of alpha monitor is sensitive to alpha while discriminating against high gamma radiation.			This type of detector has been prototyped.		
Alpha Printer: Same as alpha monitor except it measures, washes, and dries samples before counting.	Total alpha from various emitters; used principally for detection of Pu at low concentrations (in aqueous solutions).	Good at Hanford; system is a complex electrical–mechanical device. Abandoned by SRP.	Development completed; effort required to simplify system. SRP has replaced all such units.	±15%	10^{-6} to 0.1 g of Pu/liter 5×10^{-5} μc/ml
Colorimeter: Measures current from phototube caused by absorption of visible light in solution; depends upon specific wavelength absorption of various substances; absorption is proportional to concentration.	Concentration of light-absorbing materials: U, Pu, and dichromate concentrations.	Good; system is simple; subject to interference from other colored ions and decomposition products in organic materials.	Development of sampling cells and light sources fairly complete; full-stream monitors adapted for commercial units in use.	±5% ±20% ±3% ±1%	30 to 500 g of U/liter 2 to 32 g of $Cr_2O_7^{=}$/liter 26 to 55 g of U/liter 0.1 to 70 g of U/liter and 0.1 to 10 g of Pu/liter
	U in the presence of Fe. U in waste solutions.				0.1 to 2 g of U/liter 0.0002 to 0.002 g of U/liter with added reagent
Dielectric Constant: Measures change of capacitance, with solution forming part of capacitance.	% TBP in diluent electrolyte in organic.	Failed at ORNL; used in Hanford laboratories.	Development needed on instrumentation and interpretation.	±0.5%	20 to 30% TBP
	Interface level.	Used routinely in column interface control. Abandoned at SRP.	Interface control needs development for high radiation fields and removal of metal deposits.	±1/8 in.	0 to 48 in.
Conductivity: Measures resistance of solution with an a-c bridge; conductivity is proportional to concentration of electrolyte.	Concentration of electrolyte in solution, e.g., other measurements plus conductivity can determine concentration of acid and U in water; can be used to measure liquid level also	Excellent; simple system; can be used directly in stream or vessel; no sampling needed.	Instruments commercially available; continuous in-line acidity measurements being made.	±7% <0.03*M* ±0.2*N*	0.01 to 10^{6} ohms 0.1*M* to 0.4*M* HNO_3 0.1 to 0.9/ohm-cm
Gamma Absorptiometer: Measures current from ion chamber or scintillation detector caused by gamma radiation from a fixed source; radiation is absorbed by solution components in proportion to concentration and mass absorption coefficient.	Concentration of heavy elements: U, Pu, and Th; will not distinguish between these elements; practically unaffected by light-element concentration.	Excellent; system is simple; can be installed in-canyon because maintenance is small.	Usable instruments complete in plants. Data logging gamma absorptiometer operated over a year in pilot plant.	±7% ±0.3% ±0.5 g of U/liter	5 to 300 g of U/liter 300 to 420 g of U/liter 0 to 120 g of U/liter

(Table continues on the next page.)

Table II-3 (Continued)

Instrument and principle of operation	Variables determined	Reliability	State of development	Accuracy	Range of instruments used
Gamma Monitor: Measures current or pulses from multiplier phototube activated by light from NaI(Tl) scintillation crystal caused by interaction of gamma photons with crystal; can give total gamma, gamma-energy spectrum, or a specific gamma energy.	Total gamma activity or gamma-energy spectrum or a single gamma emitter; can be used to detect presence and quantity of gamma emitters in solids, liquids, or gases.	Good; dependent on sampling and cell decontamination.	Well advanced; in-line unit being used with 400 channel analyzer.	±15%	0.01 to 30 curies/ml (^{137}Cs or equivalent) 10^{-5} to 10^{-3} curie/ml 0 to 1.2×10^4 counts/(min)(ml) 5 decades of counts/min
Neutron Monitor: Measures current or pulses from BF_3 counters or other detectors caused by neutron interaction with light elements to produce alpha particles.	Neutrons producted by alpha–neutron reaction; alpha emitters such as U, Pu, Am, and Cm produce neutrons when in solution in proportion to concentration; analysis obtained by (α,n) reaction with light elements O,F,N, etc.; useful for Pu and ^{235}U.	Excellent; no sampling system; primary element reliable; maintenance low.	Extensive research and development needed; SRP has done considerable work; calibration and shielding need thorough study. Neutron multiplication technique developed.	±5% ±5% ±10%	~1.0 to 60 g of Pu/liter 3 to 100 g/liter 0.1 to 100 g of Pu/liter 1 to 3 g of Pu/liter 0.5 to 12 g of ^{235}U/liter
*p*H Monitor: Measures potential developed between glass and calomel electrode due to the hydrogen-ion concentration; provision made for intermittent calibration against standard solutions.	Concentration of acid or base in aqueous solutions.	Good; system is fairly simple.	Completed for operation on sampled solutions; number of continuous in-line instruments also installed.	±0.1 *p*H	0 to 14 *p*H
Polarograph: Measures current from reduction of ion to lower valence state; current is proportional to the ionic concentration of reducible species.	Concentration of various ions in aqueous solutions; especially useful for small concentrations of U.	Good, but system is quite complex; U measurement subject to interference from organics, iron, etc.	Development of plant unit well along; not suitable for full-stream monitor; cyclic but automatic; prototype installed in raw waste system.	±20%	0.02 to 6 g of U/liter 0.01 to 10 g of U/liter 0.002 to 0.02 g of U/liter 0.005 to 0.1 g of U/liter 0.02 to 2 g of U/liter
Reduction–Oxidation: Measures interelectrode potential between measuring and reference electrodes.	Valence state particularly for Pu; ionic concentration, e.g., Cl.	Probably as good as *p*H.	Instrumentation exists; a considerable amount of work needed on application and interpretation of data.		
Turbidimeter: Measures light transmitted; variation of colorimeter.	Aqueous phase dispersed in organic and vice versa.	Probably equal to colorimeter.	Instrument exists; work needed on interpretation of data and application; sampling problem.	0.2%	0 to 1% organic

is discussed briefly, and it is noted how these measurements are usually carried out in present plants. Jobe states that it is hard to justify economically the newer in-line instrumentation in present plants. However, new installations could make use of some of the concepts, and this report, along with its reference list, should make a good starting point. (D. M. Paige)

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Section

III

Reactor Fuel Processing

Research and Development on Nonaqueous Processing

Volatility Processes

Various types of processes based on the volatility of uranium and plutonium hexafluorides have been proposed for processing irradiated reactor fuels. Volatility processes are being applied to both highly enriched fuels and ceramic fuels of low enrichment. In these processes spent reactor fuels are converted to fluorides, and decontamination is carried out by distillation or absorption–desorption methods. A significant feature of several volatility processes under development for both high- and low-enrichment fuels is the application of fluidization techniques to the direct chemical conversion of fuel materials into gaseous compounds. Alternative processes for the recovery of uranium from fuel materials are the Nitrofluor and the fused-salt volatility processes.

A comprehensive summary of work on volatility processes since 1958 has been published by the International Atomic Energy Agency (IAEA) in *Atomic Energy Review*.[1]

Nitrofluor Process

The Nitrofluor process for treating spent reactor fuels is based on dissolution of the fuel in anhydrous hydrogen fluoride solutions containing complexing agents in the form of N_2O_4 or N_2O_3 with or without NOF. Uranium and plutonium, which readily dissolve in the solvent, are recovered from the fission products by volatility techniques. Recent work at Brookhaven National Laboratory (BNL)[2] has been concerned with engineering-scale demonstrations of the dissolution of U–Zr alloy fuel in the ternary azeotrope which contains NOF, N_2O_3, and HF and which boils at 95°C. Zirconium dissolves in the ternary azeotrope according to the reaction:

$$6NOF + Zr \rightarrow 4NO + (NO)_2ZrF_6$$

Hydrogen fluoride does not enter into the reaction and therefore dilutes the solvent so that, after an initial period of vigorous reaction, the reaction rate decreases markedly.

The engineering-scale studies were performed in a 6-in.-diameter Monel dissolver mounted on a 17-gal salt-receiver vessel. The heat of reaction was removed from the dissolver by circulating anhydrous HF at 20°C through an internal cooling coil. The nitric oxide (NO) gas released during dissolution was collected in a 500-gal gas receiver. The rate of pressure rise in the receiver was used to monitor the reaction rate.

A series of three dissolution tests was successfully demonstrated in the 6-in. dissolver using U–Zr alloy fuel sections weighing up to 3.8 kg. High alloy-dissolution rates (up to 300 g of zirconium per minute) were obtained during the initial reaction period (~5-min duration). The maximum fuel temperature during this period was 111°C. After each dissolution the inside of the dissolver was inspected, and in no case was any corrosion of the vessel, cooling coil, or thermocouples evident.

During the dissolution of U–Zr alloy fuel in the ternary azeotrope (weight ratio of solvent to metal of 11), the quantity of zirconium complex salt produced exceeds the solubility of the salt, and most of the zirconium appears in the form of a precipitate that readily separates from the solvent. The uranium remains in solution as $NOUF_6$. Several methods of separating uranium from zirconium have been studied and evaluated on a laboratory scale. Of the several separation methods that have been evaluated, the following technique appears to be most deserving of further study on an engineering scale: (1) evaporation of the dissolver solution which leads to the coprecipitation of the uranium and zirconium as complex salts, (2) agitation of the solid residue with liquid bromine trifluoride at

150°C which converts the uranium to volatile UF_6, and (3) condensation of all volatile material produced in step 2 in an adjacent vessel. It is expected that steps 2 and 3 will have to be performed five times in order to achieve 99% recovery of the uranium.

Laboratory-scale experiments are also being performed at BNL[2] to establish methods for separating uranium and plutonium in the processing of low-enriched fuels by the Nitrofluor process. Two techniques are being evaluated: (1) fluorination of the complex salts with BrF_3 to recover uranium as UF_6, followed by reaction with fluorine at 500 to 550°C to produce PuF_6; and (2) selective volatilization of uranium as $NOUF_6$, followed by fluorination with fluorine at 500°C to recover plutonium as PuF_6.

Volatility Processes for High-Enriched Fuels

The initial step in processing reactor fuels containing highly enriched uranium involves the separation of uranium from the fuel matrix; this frees the uranium for subsequent recovery by fluoride-volatility techniques. Several processes that involve separation methods based on the relative volatility of chlorides are being developed for U–Zr and U–Al alloy fuels. Uranium is separated from the alloy initially by converting the alloying metal to a volatile chloride. Final recovery of uranium is achieved by fluorination to produce volatile UF_6. Volatility processes are also being applied to graphite-matrix reactor fuels containing enriched uranium carbide.

URANIUM-ALLOY FUELS

A fluid-bed volatility process for recovering uranium from highly enriched uranium-alloy fuels is being developed at Argonne National Laboratory (ANL). A survey of recent developments at ANL on fluid-bed volatility processing of alloy fuel materials has been issued.[3] Much of the information described in the report has been reviewed in previous issues of *Reactor Fuel Processing*.[4–6] A thermodynamic study of the chemical reactions employed in the recovery of uranium from U–Zr alloy fuels by fluoride-volatility techniques has been published in a French report.[7]

An experimental program has been established at ANL to obtain data on the corrosion of nickel in fluoride-volatility-process environments. The results of laboratory-scale tests in which Nickel 200 plate specimens were exposed (1) to fluorine and to mixtures of fluorine and hydrogen chloride and (2) to fluorine and oxygen for periods up to 960 hr have been published.[3,8] Details of the laboratory-scale tests and corrosion-rate data are summarized in Table III-1. Each value represents an average value for four specimens. The corrosion rate of Nickel 200 plate was found to be 0.9 mil/year for an atmosphere of 50 vol.% fluorine in nitrogen at 485°C. Corrosion rates for the F–HCl environment and the F–O environment were found to be somewhat higher than the corrosion rate for the 50 vol.% fluorine environment; but the range of values (0.9 to 4.1 mils/year) indicates that only a small change in the corrosion rate occurs by alternating such a fluorine environment with either HCl or oxygen. The high corrosion rates exhibited by Nickel 200 specimens welded with weld-filler metal 61 are believed to be caused by the loss in integrity of the normally protective nickel fluoride film as the titanium in the weld filler reacts and forms a volatile material; $TiOF_2$ was found by X-ray diffraction in a condensed phase.

Both welded and nonwelded specimens were examined metallographically for evidence of intergranular penetration or localized attack in areas where high stress would be expected. No such evidence of attack was found in any specimen. Thermal cycling and exposure of samples to air (containing normal humidity) between periods of exposure to process environments had no marked effect on corrosion rates.

Preliminary evaluation of corrosion specimens mounted at various locations in the enriched-uranium-alloy pilot plant[4,6] has been completed.[3,8,9] Average corrosion rates of welded and unwelded Nickel 200 and Nickel 201 specimens mounted in the halogenation reactor were 0.10 mil/day (~35 mils/year) in the fluidized-bed region and 0.075 mil/day (~20 mils/year) in the vapor space above the bed. The higher corrosion rates observed on specimens in the fluidized bed are attributed to the removal of the protective fluoride film by the action of the fluid-bed particles.

Corrosion rates of less than 0.04 mil/day (14 mils/year) in the pyrohydrolysis reactor were exhibited by 304 and 347 stainless steel and Inconel 600. There was no marked difference in the corrosion behavior of these materials whether immersed in the fluidized bed or

Table III-1 LONG-TERM CORROSION OF NICKEL 200 PLATE AND WELDED NICKEL 200 PLATE IN GASEOUS ENVIRONMENTS§

Environment	Corrosion rate, mils/year								
	Nickel 200 plate*			Filler metal 61 welds†			Nickel 200 welds‡		
	240 hr	480 hr	960 hr	240 hr	480 hr	960 hr	240 hr	480 hr	960 hr
F_2 at 475°C§	0.9	0.9	0.9	1315	763	695	2.0	3.4	0.6
F_2/HCl at 450°C¶	2.1	1.5	0.9	67	76	70	3.3	2.2	1.1
F_2/O_2 at 500°C**	1.9	3.8	4.1	382	673	707	5.0	4.4	2.2

*Nickel 200 plate, 1/16 and 1/8 in. thick, is manufactured by the International Nickel Company, Inc., and has the following nominal composition in percent: Ni, 99.5; C, 0.06; Mn, 0.25; Fe, 0.15; S, 0.005; and Cu, 0.05. The corrosion rate was calculated by obtaining the weight loss of the specimen after defilming and by assuming that the film had formed uniformly on all exposed surfaces of the specimen.

†These specimens were made of two pieces of Nickel 200 plate, 3/16 in. thick, welded together using nickel filler metal 61 and the Inert Gas Tungsten Arc (TIG) process. The filler metal is manufactured by the International Nickel Company, Inc., and has the following nominal composition in percent: Ni, 93.0; C, 0.05; Mn, 1.0; Fe, 1.0; S, 0.01; Si, 0.75; Cu, 0.25; Al, 1.50; Ti, 2.0 to 3.5; and other, 0.50. The corrosion rate was calculated by determining the weight loss after defilming and by assuming that this was lost uniformly from the original weld area.

‡These specimens were made of two pieces of Nickel 200 plate, 3/16 in. thick, welded together by the TIG process using Nickel 200 filler metal. The corrosion rate was calculated by determining the weight loss of the specimen after defilming and by assuming that this was lost uniformly from the total specimen area.

§Specimens were held at 475 ± 35°C in an atmosphere of 50 vol.% fluorine in nitrogen at about 1000 mm Hg absolute. Gas velocity past coupons was about 0.002 ft/sec.

¶Specimens were held at 450 ± 10°C in an atmosphere of 50 vol.% fluorine in nitrogen alternated with an atmosphere of 50 vol.% HCl in nitrogen every 24 hr. System pressure and gas velocity were similar to those listed in footnote § above.

**Specimens were held at 500 ± 25°C in an atmosphere of 50 vol.% fluorine in nitrogen alternated with an atmosphere of 50 vol.% oxygen in nitrogen every 24 hr. Flow conditions were similar to those listed in footnote § above.

suspended above the fluid bed. Both Inconel and nickel-sintered-metal filters were entirely satisfactory for use in the $HCl-H_2O-H_2$ off-gas from the pyrohydrolysis reactor.

GRAPHITE-MATRIX FUELS

Engineering-scale investigations on methods for processing graphite–uranium carbide fuels are being conducted at BNL[2] and Oak Ridge National Laboratory (ORNL).[10] These studies are applicable to the High Temperature Gas Cooled Reactor (HTGR) fuel or other fuels containing uranium carbide in a graphite matrix. The proposed processing scheme consists basically of oxidation of the graphite and uranium carbide by oxygen to convert the graphite to CO and CO_2 and to convert uranium, thorium, and other materials to their respective oxides. The nonvolatile oxide ash is then treated by aqueous dissolution or fluoride-volatility techniques for the recovery of uranium.

A facility has been constructed at BNL[2] for demonstrating the fluid-bed oxidation–fluorination process for the recovery of uranium from uranium carbide–graphite fuel. A description of the BNL facility and results of demonstration tests with UC–graphite fuel were presented in the Spring 1965 issue of *Reactor Fuel Processing*.[11] Recent work[2] has concerned the processing of HTGR fuel, which consists of $(U-Th)C_2$ microspheres coated with pyrolytic carbon and dispersed in a graphite matrix. Demonstration of the oxidation step was performed in a 2-in.-diameter nickel fluid-bed reactor containing 1530 g of alumina particles. The fluid bed was divided into two sections by a fuel-support grid. The fuel material was periodically charged to the bed through a line located at the top of the reactor. The oxidation reaction was carried out using 100% oxygen at a flow rate of 1 scfm at bed temperatures of 725 to 800°C. Fuel material was added to the reactor as required to keep the oxygen utilization high, the frequency of addition being based on the CO_2 and CO concentration in the off-gas stream. The CO_2 concentration in the off-gas increased with an increase in the bed temperature, whereas the CO content was relatively unaffected by bed temperature. The time required to oxidize 1152 g of fuel was approximately 6 hr.

Recovery of the uranium as UF_6 from the ash was accomplished by a 2-hr fluorination with 25 to 50 vol.% fluorine in nitrogen at a bed temperature of 450 to 550°C. On the basis of the uranium concentration in the alumina-bed ma-

terial, approximately 98% of the uranium was converted to UF_6 in this single demonstration test.

Workers at ORNL[10] have recently studied the oxidation and fluorination of uranium carbide–graphite fuels in a 4-in.-diameter fluid-bed reactor constructed of Nickel 201. The reactor (Fig. III-1) is divided into two sections by a perforated fuel-support grid located 2 ft above the bottom. Oxygen as the fluidizing gas is introduced through a ball-check gas distributor in the conical bottom of the reactor. Crushed fuel and inert alumina particles are introduced into the reactor above the fuel-support grid. The off-gas from the reactor is filtered through two stainless-steel filters equipped with an automatic blowback system. Ash is withdrawn from the bottom of the reactor through a screw conveyor.

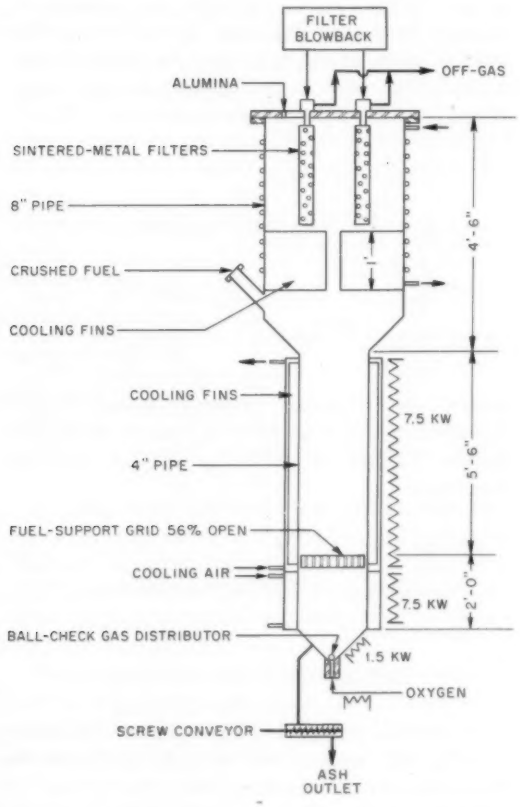

Fig. III-1 Four-inch-diameter fluidized-bed burner for pilot-plant studies.[10]

Combustion of the fuel is initiated at a bed temperature of 650°C, and the primary conversion is conducted at 700 to 750°C. Oxidation rates of 1.1 to 1.4 kg of carbon per hour have been achieved in the 4-in.-diameter reactor at oxygen flow rates of 1.3 to 1.6 scfm. Oxygen utilization decreased from 97 to 90% as the flow rate was increased from 1.3 to 1.6 scfm. As the fuel particles are oxidized, a fine particulate oxide is produced which causes a decrease in the quality of fluidization and makes it necessary to add coarse alumina particles (60 to 100 mesh) periodically to maintain proper fluidization characteristics in the reactor. An average heat flux, based on the inside surface of the reactor, of 4800 Btu/(hr)(sq ft) has been achieved. A heat-transfer coefficient from the fluid bed to the reactor wall of 85 Btu/(hr)(sq ft)(°F) has been calculated for the system.

Preliminary fluorination tests using prototype HTGR fuel have been conducted[10] in the 4-in.-diameter reactor. The fuel material was burned in the fluid-bed reactor at 725 to 800°C and produced an ash bed containing 14 wt.% ThO_2, 3 wt.% U_3O_8, and 83 wt.% Al_2O_3. The bed was fluorinated at 450 to 550°C with a gas stream containing 25 to 50 vol.% fluorine in nitrogen. Uranium recoveries of 92.1 and 98.8% were achieved after fluorination times of 2.4 and 3.8 hr, respectively. A highly exothermic reaction was observed when the bed temperature exceeded 500°C, and control over the reaction was achieved only by decreasing the fluorine concentration in the fluidizing gas. Since only a small quantity of UF_6 is evolved at temperatures below 500°C, operation in the range of 500 to 550°C appears mandatory if acceptable uranium recoveries are to be achieved. It was observed that the concentration of ThF_4 in the alumina bed must be held below 38 wt.% to avoid caking of the bed. Preliminary fluorination tests indicate that high-density ThO_2–UO_2 microspheres (96% ThO_2–4% UO_2) prepared by the sol–gel process were unaffected by fluorine at 480°C; at 650°C only 15% of the uranium was converted to UF_6 in 4 hr, which is equivalent to a radial penetration of 6 μ.

Volatility Processes for Low-Enriched Fuels: Processing of UO_2 Fuels

A fluid-bed fluoride-volatility process is being developed at ANL[3] to recover uranium and plutonium from spent uranium oxide fuel. In

this process, uranium and plutonium oxides are fluorinated with fluorine to produce volatile uranium and plutonium hexafluorides which are subsequently decontaminated and separated from one another. Details of a material flow sheet describing the ANL fluid-bed fluoride-volatility process for the recovery of uranium and plutonium from spent oxide fuel were presented in the Summer 1965 issue of *Reactor Fuel Processing*.[12]

In the fluoride-volatility process, declad UO_2 pellets are fluorinated to UF_6 in a fluidized–packed bed system using a two-zone oxidation–fluorination technique. Details of this method for treating UO_2 fuels have been published by Anastasia and Mecham.[13] In this method, oxidation of the oxide fuel occurs in the lower section (oxidation zone) of the fluid bed. The U_3O_8 fines formed in the oxidation zone are transported by the fluidizing gas to the upper section (fluorination zone) of the fluid-bed reactor, where they are fluorinated in a fluorine gas stream introduced into the reactor at a point just above the oxidation zone. In the two-zone system, the less exothermic oxidation reaction occurs in the fluidized–packed bed, and the highly exothermic fluorination reaction occurs in the upper fluid-bed section where heat-transfer coefficients are significantly higher than in the fluidized–packed bed section.

Several methods of improving the transport of U_3O_8 fines from the oxidation zone to the fluorination zone were investigated;[13] pulsation of the fluidizing gas stream appeared most successful in demonstration tests. With the pulsed system, 9-kg batches of UO_2 pellets were processed in 12 hr at 500°C. Average production rates of 50 lb of UF_6 per hour per square foot of reactor cross-sectional area and fluorine utilization efficiencies of 75% were achieved.

Preparation and Properties of Fluorides

URANIUM PENTAFLUORIDE

A method for preparing alpha uranium pentafluoride, based on the reduction of uranium hexafluoride by hydrogen bromide according to the reaction $2UF_6 + 2HBr \rightarrow 2UF_5 + 2HF + Br_2$, has been described by Wolf, Hobbs, and Rapp.[14] The reaction takes place rapidly in the gas phase with an excess of UF_6 at 65°C to produce a solid crystalline UF_5 product. The product was exposed to UF_6 for 15 hr at a pressure of 2.5 atm and a temperature of 200°C to ensure reconversion of other intermediate uranium fluorides that may have been formed to UF_5. The pure UF_5 product appeared as a chalky, light-blue powder that was characterized by X-ray diffraction to be polycrystalline alpha uranium pentafluoride.

The vapor pressure of alpha UF_5 has been determined[15] by measuring the transpiration rates over the temperature range 282 to 412°C. These experiments were performed using UF_6 as the carrier gas under sufficient pressure to prevent disproportionation of the UF_5. The melting point of UF_5 was experimentally determined to be 348°C. The vapor pressure–temperature relations obtained were:

Solid UF_5,

$$\log p = -\frac{(8001 \pm 664)}{T} + (13{,}994 \pm 1.119)$$

Liquid UF_5,

$$\log p = -\frac{(5388 \pm 803)}{T} + (9.819 \pm 1.236)$$

where p is the vapor pressure in millimeters of mercury and T is the temperature in degrees Kelvin. Calculated values for heat of vaporization were:

For the solid,

$$\Delta H_{vapor} = 36.6 \pm 3.0 \text{ kcal/mole}$$

For the liquid,

$$\Delta H_{vapor} = 24.7 \pm 3.8 \text{ kcal/mole}$$

A method for preparing fluoride complexes of UF_5 with ammonium or alkali fluorides was described in the Summer 1964 issue of *Reactor Fuel Processing*.[16] A recent paper[17] discusses the synthesis and crystallographic properties of single crystals of alkali U(V) fluoride complexes.

THERMODYNAMIC PROPERTIES OF FLUORIDES

A program is under way at ANL to determine thermodynamic properties of substances of interest in the fields of high temperature and atomic energy by the use of fluorine-bomb calorimetry. Recent work[3] has concerned the measurement of the enthalpies of formation of PF_5, SF_6, SeF_6, MgF_2, YF_3, and AlF_3. The values ob-

tained from combustion of the elements in fluorine were:

	$-\Delta Hf^\circ_{298}$, kcal/mole
P (triclinic, red) + $\frac{5}{2}F_2$ (gas) → PF_5 (gas)	376.7 ± 0.4
S (rhombic) + $3F_2$ (gas) → SF_6 (gas)	291.8 ± 0.2
Se (monoclinic, black) + $3F_2$ (gas) → SeF_6 (gas)	266.8 ± 0.2
Mg (crystal) + F_2 (gas) → MgF_2 (crystal)	268.7 ± 0.3
Y (crystal) + $\frac{3}{2}F_2$ (gas) → YF_3 (crystal)	410.7 ± 0.8
Al (crystal) + $\frac{3}{2}F_2$ (gas) → AlF_3 (crystal)	361.1 ± 0.6

Greenberg and associates[18] have measured the energies of formation of niobium and tantalum pentafluorides by direct combination of the elements in a bomb calorimeter. The derived standard thermal data for the formation of NbF_5 (crystal) and TaF_5 (crystal) at 25°C are:

	NbF_5 (crystal)	TaF_5 (crystal)
Energy of formation ($\Delta Ef^\circ = \Delta Ec^\circ$), kcal/mole	−432.02 ± 0.15	−453.49 ± 0.19
Enthalpy of formation (ΔHf°), kcal/mole	−433.50 ± 0.15	−454.97 ± 0.19
Entropy of formation (ΔSf°), cal/(deg)(mole)	−91.5	−90.4
Gibbs energy of formation ($\Delta Gf^\circ = \Delta Hf^\circ - T\Delta Sf^\circ$), kcal/mole	−406.22 ± 0.15	−428.02 ± 0.19

In other work Domalski and Armstrong[19] have reported the heat of formation of aluminum fluoride by direct combination of the elements. The value obtained, −360.37 ± 0.29 kcal/mole, is in good agreement with the value, −361.1 ± 0.6, obtained at ANL.[3]

Workers at BNL[2] have calculated the free energies of formation of several fluorides at 600°C by galvanic-cell electromotive-force measurements. The molar values obtained are:

ThF_4, $\Delta F^\circ = -436.2$ kcal	AlF_3, $\Delta F^\circ = -305.7$ kcal
NiF_2, $\Delta F^\circ = -126.8$ kcal	PbF_2, $\Delta F^\circ = -130.9$ kcal
CoF_2, $\Delta F^\circ = -129.6$ kcal	UF_3, $\Delta F^\circ = -310.5$ kcal

In a recent publication Feber[20] has compiled the heats of dissociation at 298.15°K of the gaseous halides of elements with atomic number above 19.

PREPARATION AND PROPERTIES OF FLUORIDES

Muetterties and Tullock[21] have published a detailed review of the major preparative procedures that have been reported for inorganic fluorides. Over 300 references to the literature are cited in the review article. A comprehensive review of the chemistry of hexafluorides has been published by Weinstock.[22]

A method for preparing metal fluorides by reaction of powdered metal with fluorine in a fluidized-bed reactor has been disclosed by Roesky and associates.[23] The technique has been successful in the preparation of MnF_4, PbF_4, BiF_5, and ReF_7.

Edwards[24] has prepared and characterized chromium pentafluoride and chromium oxide tetrafluoride ($CrOF_4$). Chromium pentafluoride is a crimson solid that melts at 30°C to a dark-red viscous liquid. The $CrOF_4$ is dark red, and its melting point is 55°C. Gillespie and Quail[25] have observed that iodine heptafluoride reacts with silica at 100°C to form iodine oxide pentafluoride (IOF_5). This material is a colorless liquid at room temperature and has a melting point in the range −10 to −20°C.

The vapor pressure of ZrF_4 has been measured in the temperature range 681 to 913°K by means of a mass spectrometer.[26] The temperature dependence of the experimentally determined vapor pressure was described by the equation

$$\log p = 13.5571 - \frac{12430}{T}$$

(J. J. Barghusen)

Processing of Molten Fluoride Salts of the ORNL Molten Salt Reactor Experiment

Facilities have been installed at ORNL[27] for nonaqueous processing of the molten fluoride salts of the Molten Salt Reactor Experiment (MSRE), which has recently gone critical.[28] In this experimental reactor system, the reactor fuel is a molten $LiF-BeF_2$ salt containing enriched uranium as dissolved UF_4. The $LiF-BeF_2$ salt is also used for cooling and for flushing the reactor. The reactor concept, the fuel properties, the relation of the processing facilities to the system as a whole, and the costs of the processing plant were reviewed in the Spring 1965 issue of *Reactor Fuel Processing*.[29]

The nonaqueous processing plant has two functions. The first is to convert any oxides in the molten salts to fluorides by sparging with hydrogen fluoride and hydrogen. The second is to recover uranium by sparging with fluorine and volatilizing uranium as UF_6. The elimina-

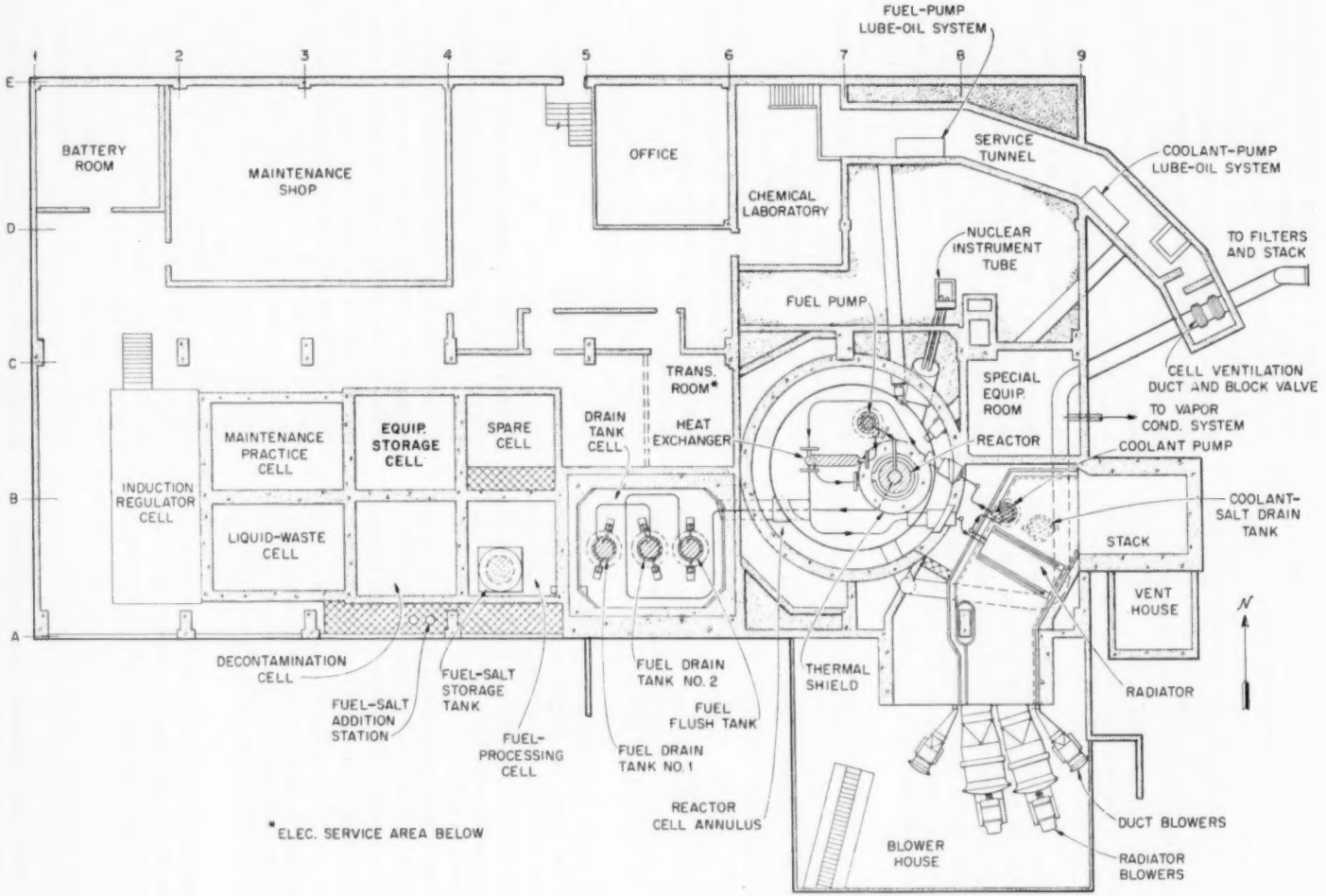

Fig. III-2 First-floor plan of MSRE building.[27]

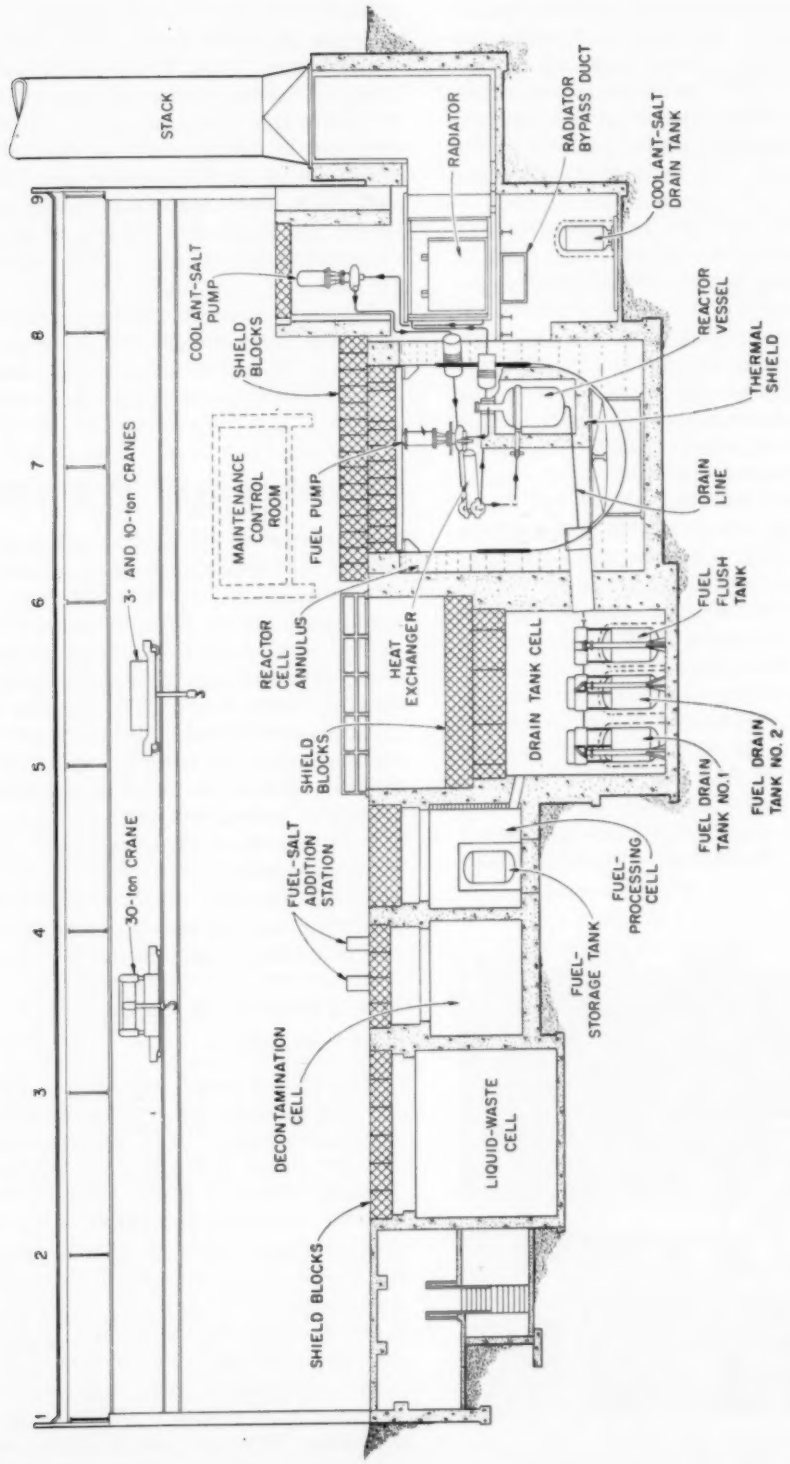

Fig. III-3 Elevation drawing of MSRE building.[27]

tion of oxide is necessary to prevent precipitation of solids in the reactor system; the recovery of valuable enriched uranium is necessary before the salt, containing fission products, can be discarded to waste. A flow diagram of the MSRE fuel-processing system[27] was shown in the Spring 1965 issue of *Reactor Fuel Processing*.[29]

The spent salt from the reactor system is held for processing in a fuel-storage tank. In the treatment with H_2–10% HF at 1110°F, the off-gas passes through a caustic scrubber and an activated-charcoal trap. The caustic scrubber removes HF from the gas, and the charcoal removes any volatile tellurium (as H_2Te) or iodine (as HI). Under these processing conditions, no significant amounts of other constituents are expected to be volatile.[27]

In the treatment with fluorine at 840°F, the off-gas containing UF_6 is put through a sodium fluoride bed at 750°F to remove niobium, chromium, zirconium, and other contaminants. The final separation of UF_6 from fission products and noncondensable gases is effected in a series of absorption–desorption cycles, using disposable containers filled with sodium fluoride. Excess fluorine is converted to the nonreactive compound SO_2F_2, and removal of residual fission products from this gas is provided by the caustic scrubber and the activated charcoal. The effluent gas is passed through an absolute filter before discharge to the atmosphere via a 100-ft stack.

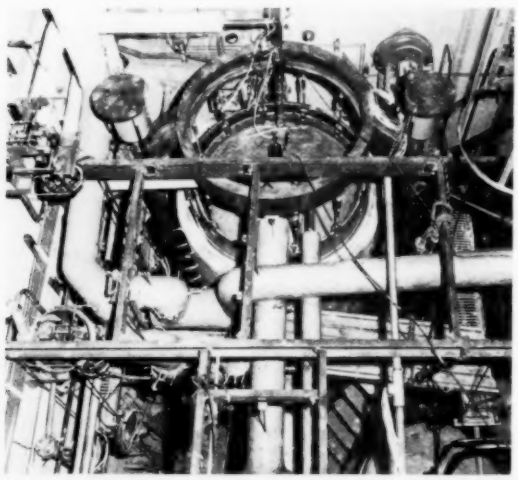

Fig. III-4 The MSRE fuel-processing cell.[27]

Corrosion of the fuel-storage tank, constructed of INOR-8 (71 wt.% nickel, 16 wt.% molybdenum, 7 wt.% chromium, and 5 wt.% iron), is slight during the H_2–HF treatment, but corrosion rates of up to 0.5 mil/hr are expected in the fluorination step. The storage vessel is 50 in. in diameter and 116 in. high, with ½-in.-thick sides and ¾-in.-thick dished heads. The total tank volume of 117.5 cu ft is designed to operate with a 38% freeboard above the salt.

Details of equipment design, plant layout, and operating procedures are given in Ref. 27. Views of the plant are shown in Figs. III-2 to III-4. A safety evaluation is included in the report.[27] (W. J. Mecham)

Pyrochemical Processes

Pyrochemical processes are nonaqueous processes for the recovery and purification of partially burned reactor fuels. In these processes extensive use is made of molten-metal and molten-salt systems as processing media. However, processes are also available for handling metallic fuels directly, i.e., without dissolution in any solvent media. Advantages of these processes include (1) their ability to handle short-cooled high-burnup fuels, which makes a fuel-inventory reduction possible; (2) their suitability for use in small plants serving one or a few nearby reactors; (3) decrease in criticality problems because of the absence of aqueous solutions; and (4) direct production of concentrated fission-product wastes.

EBR-II Fuel Cycle Facility and Operations

The EBR-II Fuel Cycle Facility is now in routine operation for recovering and recycling fuel discharged from ANL's Experimental Breeder Reactor No. 2 (EBR-II) at the National Reactor Testing Station in Idaho. Built adjacent to the reactor, the fuel-recovery facility provides the first practical demonstration of a closed fuel cycle, i.e., a cycle in which recovered and refabricated fuel is returned to the reactor. The first subassembly fabricated from recovered fuel was returned to the reactor in April.[30]

No difficulties have been encountered in recovering discharged EBR-II fuel by melt refining. This process involves melting the discharged fuel in a lime-stabilized zirconia

crucible; holding it at a temperature of 1400°C for about 3 hr to allow release of fission gases and removal of rare-earth, alkali, and alkaline-earth fission products by selective oxidation; and then pouring the purified metal into a mold. The cast ingot is the starting material for fuel-refabrication operations. The melt-refining pouring yields have been high (93 to 95%) for all batches of fuel discharged to date.[31] Fuel with a burnup of as high as 0.8 at.% of the heavy elements and with a cooling time of only about 15 days has been processed.[32] The reactor[33] is currently operating at a power level of 45 Mw(t). At this power level, and for a fuel burnup of 1 at.% and a reactor operating factor of 0.6, a processing rate of about 3 kg of fuel per day is required. Since about 10 kg of fuel is processed in each melt-refining run, one melt-refining run must be made every three days. The rate of processing varies directly with power level and operating factor and inversely with burnup.

After a melt-refining run, the crucible residue (skull) is oxidized and stored until it can be processed for recovery of the fissionable-material values. When one of the crucible residues was oxidized, a glow was noticed on the inside of the crucible just above the melt line[31] (previous crucibles had not been inspected). The fuel had a maximum burnup of between 0.44 and 0.50 at.%, and the total time between fuel discharge and skull oxidation was three weeks. It appears that the glow is not a thermal effect but some other effect, possibly a radiation-induced fluorescence, resulting from deposition of fission products above the melt line. After the oxides had been dumped, the crucible and oxides had activity levels at 1 ft of 50,000 and 40,000 r/hr, respectively.

Except for problems inherent in beginning remote operations with irradiated fuel, the refabrication operations of injection casting, pin processing, fuel-element assembly, welding, and bonding are generally satisfactory.[30]

Halide Slagging

Development work has been completed at ANL on a modification of the melt-refining process that involves the use of a chloride flux (halide slagging). The process could be used to achieve either or both of two objectives: (1) selective extraction of lanthanons and other electropositive fission products from a molten fuel alloy (uranium and U–Pu base alloys) into an overlying $CaCl_2$ flux containing a small amount of $MgCl_2$ oxidant, and (2) extraction of plutonium from a U–Pu alloy (blanket material) into a $CaCl_2$ flux containing a UCl_3 oxidant. Work on the first of these objectives is reported in Refs. 34 and 35. References 36 and 37 give recent information on the extraction of plutonium.

Equilibrium constants have been determined for the reaction

$$UCl_3(CaCl_2) + Pu(U) \rightleftharpoons PuCl_3(CaCl_2) + U$$

The materials were contained in a beryllia crucible. The variables investigated were temperature (1150 and 1200°C), initial plutonium concentration in the uranium (0.2 to 4.2 wt.%), time (15 to 90 min), and ratio of UCl_3 to plutonium (~1 to 18). The equilibrium constant was found to be approximately 200 at 1150 and 1250°C. This value is sufficiently high that satisfactory separation of uranium from plutonium should be achieved in one equilibrium stage. The free-energy changes for the reaction are −15.1 kcal/mole at 1150°C and −15.2 kcal/mole at 1200°C (assuming all activity coefficients to be unity). Changes in the initial plutonium concentration and the ratio of UCl_3 to plutonium had no effect on equilibrium, which was attained in 15 to 30 min. Uranium and plutonium material balances were good, 97.1 to 101% for plutonium and 99.2 to 99.8% for uranium, but a correction had to be made for a small amount of plutonium removed in a reaction layer that formed between the wall of the beryllia crucible and the melt. In the presence of flux, the rate of reaction of the molten alloy with the beryllia crucible (~150 $\mu g/cm^2$ in 45 min) was roughly an order of magnitude greater than in the absence of flux.

The development of this process has been taken to a point where it can be evaluated along with other processes for specific fuel-recovery problems. No further development is planned until a specific need arises.[38]

EBR-II Skull-Reclamation Process

The skull-reclamation process is presently under development for recovering uranium from oxidized melt-refining crucible residues. Plant equipment for this process (scale, ~4.25 kg of uranium) is presently being tested at the Argonne, Ill., site of ANL for later installation in the Fuel Cycle Facility. Pilot-plant studies on

a scale of 1.5 kg of uranium are nearing completion.[38]

An alternative flow sheet,[38] which provides considerable simplification both in process and equipment operation, has been investigated in the pilot plant. The flow sheet (Fig. III-5) has two steps less than the previous flow sheet published in the Winter 1963–1964 issue of *Reactor Fuel Processing*.[39] The equipment requirements are the same for both flow sheets. Also, in both flow sheets the relatively noble fission-product elements are first extracted into zinc from a suspension of the skull oxides in a halide flux. The zinc phase is then discarded to waste. In the alternative flow sheet, the uranium oxides are then reduced by magnesium contained in a 60 wt.% Mg–Zn reducing solution. Uranium metal precipitates almost completely out of the reducing solution. Rare-earth and alkaline-earth elements that remain in the flux and supernatant metal phases are removed and discarded. The precipitated uranium is redissolved in a Zn–14 wt.% Mg solution, and the product solution is transferred to the retorting operation.

The advantages claimed[38] for the alternative flow sheet are as follows:

(1) Two steps of the previous flowsheet (the intermetallic precipitation and decomposition steps) are eliminated, thereby shortening the flowsheet.

(2) Operating time is reduced by a factor of two or three. This is brought about not only by the shortened flowsheet but also by eliminating temperature cycles which, in the original flowsheet, required considerable time to effect. Once the equipment is at temperature, it should be easily possible to process a batch of material within 8 hr.

(3) Equipment operation is simplified.

(4) Reagent consumption and waste volumes are substantially reduced.

(5) Uranium recovery is increased.

(6) For equipment of the same size, process batch sizes may be increased by 60 to 100%.

No operational difficulties were encountered in two runs made to test this flow sheet. Uranium recovery was near 100%. With the possible exception of zirconium, fission-product removals should not be adversely affected by the use of the shortened flow sheet. The behavior of zirconium under conditions of the new flow sheet is being determined.

Processes for Future Types of Reactor Fuels

Pyrochemical processes are under development at ANL for processing fast breeder reactor fuels of the ceramic (e.g., oxide and carbide) or metallic types. In these processes, fission products are separated from fissionable and fertile elements, such as uranium, plutonium, and thorium, by two major operations: (1) selective oxidation of uranium, plutonium, and thorium (and the more easily oxidized fission products) to chlorides and their transfer to a molten-halide-salt phase, leaving in the metal phase the relatively noble fission prod-

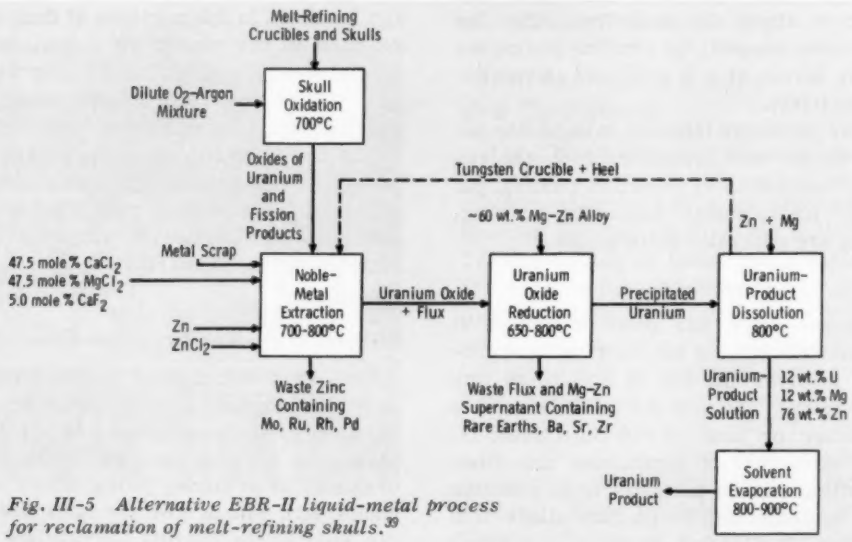

Fig. III-5 Alternative EBR-II liquid-metal process for reclamation of melt-refining skulls.[39]

ucts such as ruthenium, molybdenum, palladium, and technetium; and (2) selective reduction of uranium, plutonium, and thorium chlorides to metals and their transfer to a solvent-metal phase, leaving in the salt phase the highly reactive fission products (rare earths and alkaline earths). (A patent on the latter separation procedure has been issued to Knighton and Steunenberg.[40]) The uranium, plutonium, and thorium are recovered from the solvent metals (usually ternary alloys of cadmium, zinc, and magnesium) by vaporizing the solvent metals. The product elements can then be converted to the desired type of fuel by conventional procedures.

The application of pyrochemical separation procedures to the processing of HTGR fuel, a mixture of thorium and uranium dicarbides, has been considered briefly.[41] A conceptual flow sheet devised for processing HTGR fuel makes use of fluid-bed and pyrochemical processes for purification and recovery of the fuel and reconversion to the final carbide form. In the first steps of the flow sheet, fluid-bed oxidation and chlorination of the fuel are carried out; then the pyrochemical steps are employed. These consist of two successive selective reduction steps, the first for the separation of elements more noble than uranium and thorium and the second for the separation of the uranium and thorium from more reactive elements (i.e., rare earths and alkaline earths). Countercurrent extractions with appropriate metal and salt phases are required to achieve both high recovery of uranium and thorium and high removal of rare-earth elements. Mathematical relations and graphical methods for determining the number of stages required to effect a given separation have recently been published by Chiotti.[42] Previous reviews of this work are given in Refs. 43 and 44.

The feasibility of the pyrochemical steps for processing HTGR fuel was established by an experiment in which batch extractions were employed rather than batch countercurrent or continuous countercurrent extractions.[41] Cadmium-base metal solvents containing small percentages of zinc and magnesium were contacted with a halide salt consisting of 30 mole % NaCl, 20 mole % KCl, and 50 mole % $MgCl_2$. The results of the experiment indicated the following:

(1) Excellent separation of uranium and thorium from noble metals is possible.

(2) Distribution coefficients for uranium, thorium, and cerium (a representative rare earth element) are such that high recovery of uranium and thorium and excellent separation from rare earths and alkaline earth elements can be achieved in a relatively small number of extraction stages.

(3) The pyrochemical steps should be easy to perform by either batch or continuous operations.

In one step of the cadmium-based flow sheets for the processing of high-plutonium breeder reactor fuels, cadmium metal is chlorinated in the presence of a molten salt consisting of a mixture of alkali and alkaline-earth chlorides to regenerate $CdCl_2$, which serves as an oxidizing agent. In this chlorination step a lower valent cadmium chloride has been observed and is being investigated.[41] The reaction

$$Cd + xCdCl_2 \rightleftharpoons Cd(CdCl_2)_x$$

has been studied by equilibrating liquid cadmium with $CdCl_2$ in molten LiCl at 650°C. Within experimental uncertainty, spectrophotometric measurements indicate that the value of x in the preceding equation is 2.

A purification process involving transfer of solutes between two metal alloys in mutual contact with a molten salt has been described by Chiotti and Klepfer.[45] The thesis on which the article was based[46] was discussed in the Summer 1965 issue of *Reactor Fuel Processing*.[47] The work indicated that thorium dissolved to a 40 wt.% concentration in magnesium was effectively decontaminated from yttrium and rare-earth impurities by transfer of the latter to a 4 to 8 wt.% Mg–Zn alloy through a LiCl–KCl eutectic containing 25 wt.% $MgCl_2$ as an oxidizing agent. (L. Burris, Jr.)

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Section

IV

Reactor Fuel Processing

Waste Disposal

Treatment of Low- and Intermediate-Level-Activity Wastes

Ion Exchange

At Oak Ridge National Laboratory (ORNL), a new process for the treatment of low-level-activity aqueous-waste solutions is being studied.[1] The process, known as the water-recycle process, is expected to make available for use within a nuclear installation water that has been obtained from the treatment of low-level-activity wastes. The water will be demineralized by the new process, and its radionuclide content will be 2% of the maximum permissible concentration for water (MPC_W). (As part of the process concept, all raw water entering an installation would be demineralized before use.) After the demineralized water has been used, the salt content is expected, in general, to amount to about 10 to 20% of the original salt content in the raw water.

The water-recycle process consists in the following steps:

1. A batch coagulation and clarification step to remove radiocolloids and suspensoids. This step is carried out at a *p*H of about 7 with zeta-potential-controlled* additions of alum coagulant and activated-silica coagulant aid.

2. A demineralization step to treat the supernatant solution from the first step. If additional removal of radioactive species such as ruthenium and cobalt is needed, a second sorptive step that utilizes activated carbon can be carried out.

*Zeta potential keeps particles in suspension and hinders or prevents their agglomeration.

A comparison of the economics of the water-recycle process with that of a scavenging–precipitation ion-exchange process,[2] a "treat and discharge" concept, is planned. (Laboratory and pilot-plant studies of the scavenging–precipitation ion-exchange process have been successfully completed.[1] This work has shown that large volumes of slightly contaminated water wastes that are similar to ORNL low-level-activity wastes can be treated to remove all radionuclides of interest to less than 2% of the MPC_W.)

A preliminary laboratory test of the water-recycle process was made with ORNL low-level-activity wastes (*p*H, ~7) to which ^{106}Ru and ^{60}Co were added. The treatment of the low-level-activity wastes consisted in the following: successive additions of 30 ppm alum and 0.5 ppm activated silica brought about the clarification of the low-level-activity waste solution; then a mixed-bed ion exchanger (equivalent amounts of Dowex $50W-H^+$ and Dowex $1-OH^-$) was used to demineralize the clarified supernatant; and, finally, the effluent from the mixed-bed ion exchanger was passed through a column of granular activated carbon to sorb residual radionuclides. Stepwise and overall decontamination factors (DF) for the removal of ^{106}Ru, ^{60}Co, ^{137}Cs, ^{90}Sr, ^{144}Ce, and $^{95}Zr-^{95}Nb$ were determined. The overall DF's were determined at a breakthrough that corresponded to the treatment of 200 bed volumes of low-level-activity wastes. The decontamination factors were as follows:

Step	Decontamination factor					
	^{106}Ru	^{60}Co	^{137}Cs	^{90}Sr	^{144}Ce	$^{95}Zr-^{95}Nb$
Clarification	2.3	1.9	1.1	1.2	1.7	1.5
Mixed-bed ion exchange	40	2.2	55	620	8.8	>10
Activated carbon	2.3	>330	5	1.3	76	*
Overall for process	>200	>1300	300	1000	>600	>25

*Not determined because of low level of activity in ion-exchange effluent.

Foam Separation

At ORNL a pilot-plant study[1] of a scavenging–precipitation foam process[3] for removing strontium and cesium from ORNL low-level-activity wastes is being carried out. The process consists in two steps: (1) a precipitation and coagulation step for precipitating calcium and magnesium ions and reducing the interference effect of phosphates, followed by clarification in an upflow sludge-bed filter and (2) a foam-separation procedure for removing cesium and strontium. A flow sheet of the two-step process was presented in an earlier issue of *Reactor Fuel Processing*.[4]

A schematic layout of the foam-separation portion of the pilot plant is shown in Fig. IV-1.

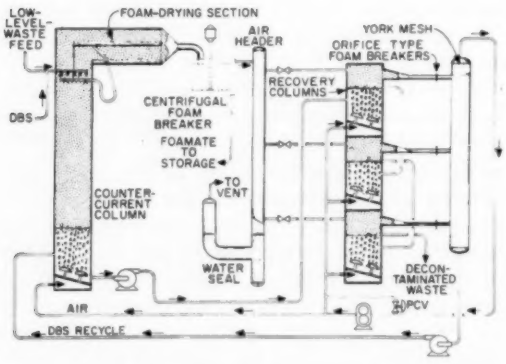


Fig. IV-1 Foam-separation portion of pilot plant for investigation of scavenging–precipitation foam process.[1]

The clarified waste, with the surfactant sodium dodecylbenzene sulfonate (DBS) added, enters near the top of the foam column and then passes down the column countercurrent to the foam produced by bubbling air through a pool of water at the bottom. The foam moves up slowly past the feed distributor and into the horizontal foam-drying section. The water drained from the horizontal section is returned to the foam below the feed distributor, and the drained foam is condensed in the centrifugal foam breaker. The decontaminated waste from the bottom of the countercurrent foam column is pumped to the DBS recovery columns, where the DBS is stripped. The recovered DBS is condensed by orifice foam breakers and returned to the bottom of the foam column for reuse. The effluent, which leaves the bottom recovery stage, is decontaminated waste water.

The complete process was demonstrated in a 93-hr pilot-plant run using ORNL low-level-activity wastes. For the scavenging–precipitation step, the operating conditions were as follows: a feed (low-level-activity wastes) rate of 5 gal/min; sodium hydroxide, sodium carbonate, and ferrous sulfate added to the low-level-activity waste to make it 0.005*M* in NaOH, 0.005*M* in Na_2CO_3, and 10 ppm in Fe^{2+}; and 0.77 lb of Grundite clay added per 1000 gal of low-level-activity wastes. For the foam-separation step, the following operating conditions were used: a feed (effluent from the first step) rate of 2 gal/min;* a DBS concentration in the feed of 120 ppm; and an air flow rate of 8 cfm. Decontamination factors for the removal of strontium were as follows:

	Decontamination factor for ^{90}Sr
Step	
Scavenging–precipitation	10
Foam separation	36
DBS recovery	3
Overall for process	>1000

The strontium concentration in the decontaminated effluent amounted to 2.3% of MPC_W. Analyses for other radionuclides are not yet available. The experimental portion of the pilot-plant study has been completed, and a topical report is in preparation.

Incorporation in Asphalt

Incorporation of intermediate-level-activity wastes in asphalt is a promising disposal method. The method, which was originated at Mol, Belgium,[5] appears to be simple, safe, and inexpensive for the storage of wastes too high in radioactivity to allow their discharge to the environment but low enough in radioactivity to prevent heat generation from being a problem. At ORNL this method is being applied to the disposal of ORNL waste-evaporator concentrate; the concentrate is produced in the processing of intermediate-level-activity aqueous wastes.[1] In recent work additional measurements were

*The capacity of the system was limited by the air-supply equipment and the centrifugal foam breaker in use at the time of the pilot-plant study.

made of leach rates of asphalt products that were produced from simulated ORNL evaporator concentrate and contained 20 or 60 wt.% concentrate solids.[6] Static and dynamic leaching tests were carried out at 25°C in distilled water. At the end of six months, the leach rate for the asphalt product containing 20 wt.% solids was the same for both types of test, 1.5×10^{-4} g/(cm^2)(day). For the asphalt product containing 60 wt.% solids, the leach rate differed for the two testing methods. It reached an apparent steady state of 3×10^{-4} g/(cm^2)(day) in static tests and about 5×10^{-4} g/(cm^2)(day) in dynamic tests. A dynamic leaching test was also conducted on an irradiated (absorbed dose of 10^8 rads) asphalt product containing 60 wt.% concentrate solids. At the end of two months, the leach rate was about the same as that of the unirradiated asphalt product containing 60 wt.% solids. This would indicate that irradiation does not affect the leach rate.

Tank Storage of High-Level-Activity Wastes

Perpetual Storage

Oak Ridge National Laboratory is preparing a detailed estimate of the costs of perpetual tank storage of aqueous wastes from the processing of power-reactor fuels.[1] [Tank-storage management of high-level-activity liquid wastes produced at various U. S. Atomic Energy Commission (AEC) installations and cost of perpetual waste storage of high-level-activity liquid wastes produced at the Nuclear Fuel Services, Inc., plant have been reported in previous issues of *Reactor Fuel Processing*.[7,8]] The results of this study will serve as a basis for comparison of costs of alternative waste-management schemes.

In this study the fuel-processing plant has a capacity of 6 tons of fuel per day and handles the fuel from an installed reactor capacity of 70,000 Mw(t). The plant processes uranium converter fuel, clad with either Zircaloy or stainless steel, and thorium converter fuel. The fuels are processed 120 days after discharge from the reactors by solvent-extraction methods. Two categories of wastes are produced:

1. Cladding wastes from the dissolution of the Zircaloy and stainless-steel cladding. These wastes are stored separately in alkaline form in tanks of about 1.1 million-gal capacity; cooling is not provided for these wastes.

2. Other high-level-activity wastes from the Purex and Thorex solvent-extraction processes. These wastes are combined and stored in tanks of million-gallon capacity which are equipped with submerged cooling coils. Storage of these wastes under both acid and alkaline conditions is considered. The tanks are similar in design to those in use at Savannah River Laboratory and are housed in steel-lined concrete vaults buried under about 10 ft of earth.[7] Tanks for containing acid wastes are fabricated of type 304L stainless steel; those for containing alkaline wastes are constructed of carbon steel.[1]

Detailed cost data now being developed will be incorporated in a computer code for calculation of storage costs.

Thermal Consequences of Leaks in Waste-Storage Tanks

In the large-scale, safe storage of high-level-activity wastes, the dissipation of heat generated by radioactive decay is taken into account in the design of storage tanks. If radioactive solution should leak from a storage tank into surrounding soil having ion-exchange capacity, high temperatures might result if the water in the leak were to evaporate or percolate away, and the heat generator would be left in dry soil which is a good insulator. If such high temperatures affected the concrete wall of the tank, larger leaks could result.

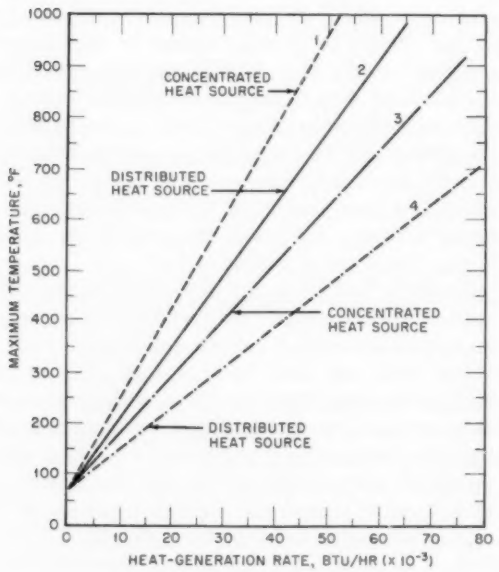
Jansen[9,10] at Hanford Atomic Products Operation has developed an analytical expression for determining the consequences of a radioactive leak into soil. Temperature rises in the soil were calculated for the hypothetical case of a leak of Purex alkaline-waste supernatant solution containing $5 \times 10^{-4} M$ ^{137}Cs [0.18 Btu/(hr)(gal)]. For a leak of 5000 gal, the maximum steady-state temperature rises would be 14°F at the concrete-soil interface and 62°F in the soil at a point 4.2 ft from the concrete liner. For a leak of 50,000 gal, comparable temperature rises would be 29 and 301°F, the latter at a point 10 ft from the concrete. Jansen concludes that even relatively large leaks of Purex alkaline-waste supernatant solution do not constitute a thermal hazard. He also presented a correlation that allows calculation of maximum steady-state temperatures for leaks of other solutions containing fission products of varying activity and adsorbability on the soil.

In-Tank Solidification of Intermediate-Level-Activity Wastes

As part of its Waste Management Program, Hanford plans to carry out the solidification of intermediate-level-activity plant-waste solutions in 75-ft-diameter underground tanks (750,000 gal each).[11] The stored wastes, which have a low heat-generation rate, will be concentrated to a salt cake up to 16 ft thick by evaporation. The evaporation will be achieved by sparging heated air directly into the waste solution. As concentration progresses, additional wastes will be routed to the tank. Prototype equipment has been installed preparatory to testing this solidification procedure.[12]

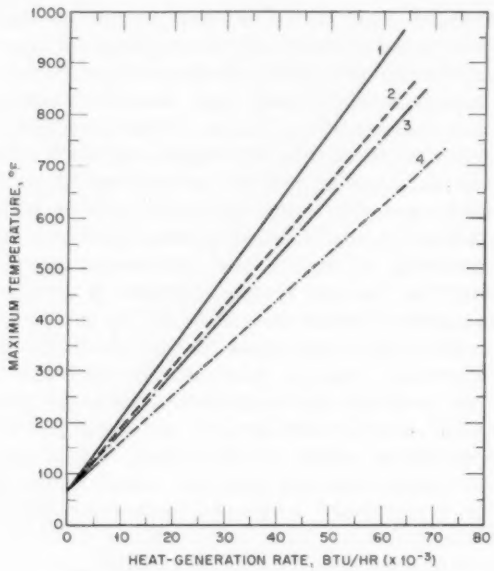
A detailed study[13] of the possible hazards associated with the in-tank solidification unit, the facility design, and processing operations has been completed. (Future in-tank solidification units and/or future wastes that might be processed by this technique were not considered in the study.) The in-tank solidification unit was judged to be basically adequate for the intended service of solidifying certain radioactive wastes for permanent storage. However, the following recommendations for the control of possible hazards were made: (1) prevent by positive means, such as decanting, the introduction of any volume of organic solvent as an immiscible phase to the in-tank solidification unit, and (2) determine the presence or absence of cyanide in the waste feed material. Cyanide compounds in tonnage amounts were introduced into Hanford underground storage tanks during a waste-scavenging program (about 1958).

Whether cyanide will be present in the waste solutions or absent, laboratory development studies are recommended to determine the con-



	K_{soil}, Btu/(hr) (sq ft)(°F/ft)	K_{cake}, Btu/(hr) (sq ft)(°F/ft)	L_{cake}, ft
1	0.15	0.33	16
2	0.15	0.33	16
3	0.33	0.33	16
4	0.33	0.33	16

Fig. IV-2 Effect of fission-product settling to a 2-ft-thick layer at bottom of tank on maximum temperature in underground tank.[14]



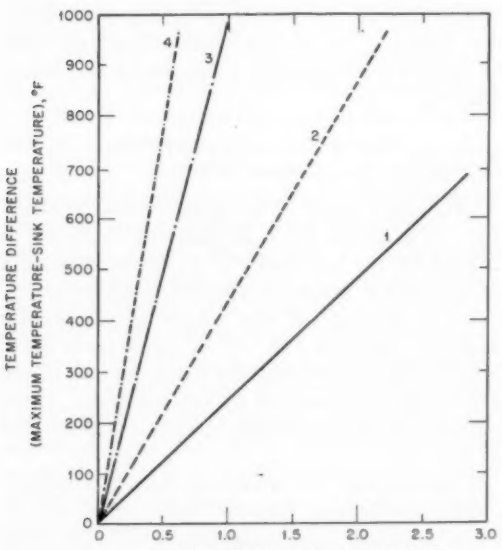
	K_{soil}, Btu/(hr) (sq ft)(°F/ft)	K_{cake}, Btu/(hr) (sq ft)(°F/ft)	L_{cake}, ft	L_{soil}, ft
1	0.15	0.33	16	11
2	0.15	0.33	16	7
3	0.15	1.20	16	11
4	0.15	1.20	16	7

Fig. IV-3 Effect of reduction in soil cover over underground tank on maximum temperature within tank.[14]

ditions and to evaluate the potential for an organic–nitrate explosion caused by the reaction between cyanide or solvent and sodium nitrate (a principal constituent of the wastes to be processed).

In support of the in-tank solidification process, a computer study of the dissipation of heat from radioactive wastes solidified in underground tanks is being carried out at Hanford.[11] The capacity of the tank for heat-generating wastes is determined by the heat-dissipation rate and the allowable maximum temperature. In recent work[14] a number of special cases have been considered. Curves are presented (Figs. IV-2 to IV-4) which relate the heat-generation rate and the maximum temperature within the tank. Figure IV-2 shows the effect, at two soil thermal-conductivity values, of settling of the heat-generating fission products to a single layer, 2 ft thick, at the bottom of the tank. Figure IV-3 indicates the effect, at two cake thermal-conductivity values, of reducing the soil cover of the buried tank from 11 to 7 ft. The effect of low soil thermal conductivity and low cake thermal conductivity for various cake thicknesses is shown in Fig. IV-4.

In other heat-transfer work at Hanford,[14] an approximate mathematical model has been developed for heat flow in a waste tank containing solidified Purex wastes. The model gives maximum temperatures that deviate, on the average, less than 5% from results calculated by an exact iterative technique.



	K_{soil}, Btu/(hr) (sq ft)(°F/ft)	K_{cake}, Btu/(hr) (sq ft)(°F/ft)	L_{cake}, ft	L_{soil}, ft
1	0.15	0.33	4	11
2	0.15	0.33	8	11
3	0.15	0.33	16	11
4	0.15	0.33	24	11

Fig. IV-4 Effect of cake thickness and low cake and soil thermal conductivity on maximum temperature in underground tank.[14]

Conversion of High-Level-Activity Wastes to Solids

Fluid-Bed Calcination

Preparation of Glass from Fluid-Bed Calcined Waste

The calcined product* from the recently completed fluid-bed calcination[15] of highly radioactive wastes (some 510,000 gal) in the Waste Calcining Facility (WCF) at the National Reactor Testing Station, Idaho, is stored underground in stainless-steel storage bins located in concrete vaults.[16] Although bin type storage at the National Reactor Testing Station is currently being considered for calcined alumina, at some future date it may be necessary to provide postcalcination treatment of the WCF calcined alumina to achieve an additional degree of safety during long-term storage.

Studies are under way at the Idaho Chemical Processing Plant (ICPP) to develop treatment methods that would reduce fission-product removal by leaching† of calcined product stored

*The WCF calcined product is made up of granular, nearly spherical alumina particles.[17] These particles have a bulk density of 1 g/cm³. The void volume within individual particles amounts to 40%. The fission products are distributed approximately homogeneously throughout the particles; the more soluble fission products can be leached if the particles are contacted with water.

†Samples of untreated, radioactive calcined alumina from the WCF were leached for seven weeks at 26°C with distilled water.[17] At the end of this period, 80% of the cesium and 40% of the strontium and less than 1% of the cerium were leached from the calcined alumina. Most of the cesium and strontium was leached in the first two or three days.

under conditions where contact with water might occur. Three different approaches[17] are being investigated: (1) fusing the calcined product with added chemicals to form a glass, (2) coating the individual calcine particles with a metallic or ceramic coating, and (3) filling the void spaces within the particles and between the particles with a solid matrix. Work on all three methods is in progress. In previously reported work[16] on the first of these methods, nonradioactive glass specimens were prepared from mixtures of calcined alumina (from a WCF cold demonstration run), sodium monobasic phosphate, and lead oxide.

In more recent work[18] the preparation of glasses from nonradioactive calcined products containing 2.5 wt.% mercury was undertaken. In the fluid-bed calcination at 400°C of aluminum nitrate type wastes containing mercury, the mercury remains with the calcined alumina. In the conversion of this calcine to glass, the mercury is expected to volatilize from the glass melt. Glass specimens were formed from this calcine; they were of a good quality and a clear, blue-green color. More than 99.9 wt.% of the mercury was found to have volatilized during fusion.

In other work[18] the effect of long-term irradiation on glasses was studied. Glass specimens produced from calcined alumina were irradiated in air to a final total dose of 10^{10} r; the equilibrium temperature of the samples was about 200°C. The total dose of 10^{10} r corresponds approximately to the cumulative irradiation that a glass prepared from WCF calcine would receive during 100 years of storage. Irradiations were conducted on glass specimens formed from mixtures with the following calcines: (1) calcine containing 2.5 wt.% mercury, (2) an excess of calcine, (3) calcine composed of 58 wt.% alpha alumina,* and (4) nonradioactive alumina calcine from the WCF.

The results of the irradiations were as follows: At 10^7 r total dose, the samples were slightly discolored, varying from yellow to tan; however, they were still clear and transparent. At 10^8 r total dose, the samples were somewhat darker in color. Two samples cracked, apparently from thermal exposure. At 10^9 r total dose, the samples were dark-brown to black; nevertheless, they were still translucent to a light beam. At 10^{10} r total dose, the samples were jet-black and opaque. The irradiation did not affect the physical integrity of the glass. X-ray diffraction analysis showed no difference between irradiated and nonirradiated portions of the same sample, which indicated the absence of extensive devitrification. Devitrification may, however, occur during preparation of the glass because of the chemical action of fission products or during the initial period of storage owing to the heat caused by decay of the fission products.

The heat-generation rate of radioactive WCF alumina calcine that was produced from highly radioactive ICPP wastes has been experimentally measured in an adiabatic calorimeter constructed of lead.[21] A rate of 0.343 ± 0.004 Btu/(hr)(lb of calcine) was found. This value was within 1.7% of the value calculated with the use of radioisotopic composition and decay data.

Fluid-Bed Calcination of Aluminum Nitrate Waste

Pilot-plant work in a 12-in.-diameter fluid-bed calciner has been initiated at the ICPP to investigate the feasibility of calcining aluminum nitrate waste solutions containing high concentrations of one of the following: zirconium fluoride,[18] sodium ion,[17,22] or ammonium ion.[21] Processing conditions are being sought which will make it possible to calcine these waste solutions with a minimum of modification to the WCF.

A pilot-plant run was made with a nonradioactive zirconium fluoride–aluminum nitrate waste solution containing added calcium ion in order to complex fluoride ion and to suppress its volatilization.[18] Operating conditions were similar to those employed in the WCF: a bed temperature of 400°C, a starting bed of alumina, a fluidizing velocity of 1.0 ft/sec, a feed rate of 10 liters/hr, and a bed pressure of slightly below atmospheric pressure. Corrosion test specimens of various materials of construction were also mounted in a number of locations in the pilot-plant calciner system. The waste solution was successfully calcined, and greater than

*The alpha crystalline form of alumina, although over 50% more dense than the amorphous form, is less resistant to attrition and is insoluble in the acidic off-gas scrubbing solution.[19,20] Since undissolved solids in the scrubbing system cause equipment erosion and plugging problems, the soluble amorphous form is favored for radioactive service. Boric acid added to the feed solution was found to inhibit the formation of the alpha form.

99% of the potentially volatile fluoride in the waste was retained in the calcined product. The calcined product is stable up to at least 800°C. This temperature is above the predicted maximum centerline temperature for calcined solids stored in bins similar to those used for WCF calcined alumina. Corrosion data show that the austenitic type stainless steels from which the WCF is constructed have negligible corrosion rates.

Radiant-Spray Calciner

At Hanford the development of radiant-heat spray calcination[23] is continuing for the treatment of high-level-activity aqueous wastes from the Purex process.[14,24] In this technique the feed solution is sprayed into the top of a heated column* where the spray droplets are converted to a powder. Two methods are being developed for handling the calcined powder. In one method the powder falls into a heated pot for completion of the calcination process. Either a sinter or melt results, depending on the composition of the residue. In the other method the powder is fed to a continuous melter for conversion to a melt or a phosphate "glass" product that is intermittently discharged to a final storage container.

Allemann, Roberts, and Upson[25] at Hanford have summarized the results of a previously reported series of radiant-heat spray-calcination pilot-plant runs[26] which were performed with plant-level-activity Purex and Redox wastes. The pilot plant was remotely operated and shielded. The spray calciner, 10 in. in diameter by 5 ft high by $\frac{1}{16}$ in. in wall thickness, was constructed of Inconel. It was used in combination with melt pots (induction heated) that were constructed of type 304L stainless-steel pipe (schedule 40), 5 in. in diameter by 13 in. high. In the course of these runs, a leak developed about midway up the wall of the spray calciner. The leak occurred subsequent to runs with feeds containing either added sulfate to produce a meltable calcine or added sugar to decompose excess nitrate and to reduce ruthenium volatilization.

*The wall of the spray calciner, which is heated autoresistively by passing a low-voltage high-amperage alternating current through the column, is maintained at 800°C. Although this method of heating is convenient for a small experimental calciner, it would probably not be employed for a plant-sized unit.

The full nature and the extent of the leak were not determined until the equipment was dismantled at the end of the radioactive experimental work.[24] The leak occurred at the vertical weld in the region of highest temperature. (The calciner had not been annealed after welding.) Figure IV-5 shows a section of the spray-calciner wall near the weld in the failure

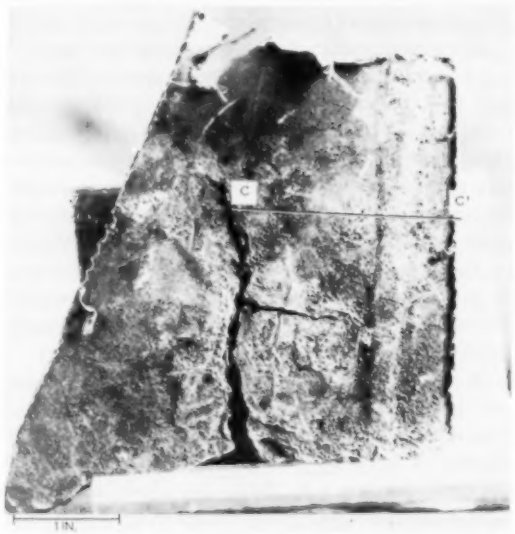


Fig. IV-5 Cracked region of Inconel calciner wall.[24] (The line indicates the cross section shown in Fig. IV-6.)

region. (The cross-sectional cut C–C′ is shown in Fig. IV-6.) The cracks would indicate that stress cracking aggravated by corrosive attack by the calcine scale may have been the cause of failure. The corrosion was localized; about 5 sq in. of area was affected. The nature of the scale is being determined. A construction material other than Inconel is planned for the

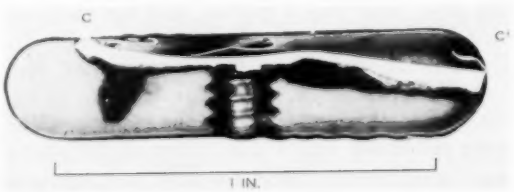


Fig. IV-6 Enlargement of cross section C–C′ of Inconel section[24] shown in Fig. IV-5.

prototype radiant-heat spray calciner to be used in the engineering-scale demonstrations of solidification processes[15] at Hanford. Type 310 stainless steel is being considered.

Nionel (a high-nickel alloy) tubing was used in the condenser in the pilot-plant off-gas system because of its corrosion resistance to nitric acid and sulfuric acid condensates.[25] After some 300 hr of process operation, none of the tubing had failed and only a small amount of corrosion had taken place.

In current nonradioactive semiworks tests,[24] a 14-in.-diameter radiant-heat spray calciner and the continuous melter were operated as a composite unit to investigate a phosphate-glass flow sheet. Two series of tests were carried out with feeds that simulated first-cycle acidic Purex-based wastes containing added phosphoric acid in varying amounts. The simulated wastes in the two series corresponded in composition to 80 gal per ton of uranium (first-cycle acid waste) and 111 gal per ton of uranium (waste produced at Nuclear Fuel Services, Inc.).

In the feeds of the first series of tests (80 gal per ton of uranium), the added phosphoric acid concentrations ranged from 0.40*M* to 0.96*M* [ratios of metallic cation (M) to phosphorus (P) between 2.9 and 1.1]. When the phosphoric acid concentrations were varied between 0.40*M* and 0.52*M* (M/P ratios of 2.9 to 2.3), calcine deposition on the calciner wall was minimal and the filter pressure drop (~15 in. of water) was acceptable. In the continuous melter free-flowing melts were produced at 950 to 1050°C. The melts cooled to crystalline solids and had densities that varied from 2.9 to 3.2 g/cm^3. When the phosphoric acid concentrations ranged from 0.63*M* to 1.0*M* (M/P ratios of 1.8 to 1.1), either the filters for the calciner became plugged or large amounts of calcine deposited on the calciner wall.

In one run of this series, long-term operation (48 hr) of the composite unit was tested with a feed containing 0.52*M* phosphoric acid. The feed rate was 5 gal/hr, and the calciner wall temperature was maintained at 700°C. The calcine deposit on the calciner wall was less than ¼ in. thick, except for one spot on the bottom conical surface where the maximum deposit thickness was 1½ in. Filter performance was exceptionally good because air blowback of the filter was used with a cleaning-cycle time of 5 min. For the entire run the overall increase in pressure drop across the filters amounted to only 1 in. of water. The continuous melter operated satisfactorily. For the calciner feed rate of 5 gal/hr, the equivalent of about 0.5 cu ft of melt per day was produced.

In the feeds of the second series of tests (111 gal per ton of uranium), the added phosphoric acid concentrations ranged from 1.15*M* to 1.73*M* (M/P ratios of 3.0 to 2.0). The calciner wall temperature was maintained at 700°C, and the melt temperatures in the continuous melter ranged from 1060 to 1125°C. Feed rates were limited to 3 gal/hr since a greater feed rate would have exceeded the melter capacity. At this feed rate the equivalent of 0.6 cu ft of melt per day was produced. The melt produced was a purple-black crystalline material and had a density of 3.3 g/cm^3. The best results were obtained in runs with feeds containing 1.15*M* or 1.28*M* phosphoric acid (M/P ratios of 3.0 and 2.7). Only very small amounts of calcine were deposited on the calciner wall. However, the pressure drop across the filters was relatively high, 22 in. of water. In a run with a feed containing 1.51*M* phosphoric acid, the results were not as satisfactory. A markedly increased amount of calcine deposited on the calciner wall. The calcine also plugged the entrance to the continuous melter and the calciner filters.

Pot Calcination

The ORNL pot-calcination process[27] is one of three processes scheduled for pilot-plant demonstration at Hanford;[28] actual high-level-activity aqueous wastes will be used in these tests. Information for the design, development, and operation of prototype pot-calcination equipment is being obtained in a cooperative program between ORNL and Hanford.

At Hanford nonradioactive testing of the prototype equipment for the pot-calcination process is being carried out.[14,24] Pot-calcination runs have been made using a six-zone 1-kc prototype induction furnace. The liquid level within a calcination pot was automatically controlled in a satisfactory manner by means of a heat-sensitive liquid-level probe. Two methods of operating the pot processes have been used. One method is referred to as cold-wall startup. It requires maintaining a full pot at all times and employs a draft tube to promote internal circulation. This delays the calcination period for a considerable period of time and keeps the operating rate high through better heat

transfer. The other method is known as hot-wall startup. It involves introducing the feed with the pot wall initially at or near the final calcine temperature (~900°C). Calcination begins almost immediately. Processing rates and overall capabilities of the two methods were shown to be nearly identical, although the initial heat input for the hot-wall method of operation is twice that for the cold-wall method.

An electrically heated pot to simulate internal heat generation was used to test the rate at which the six-zone induction-heated prototype furnace could be cooled.[24] With a total internal heat-generation rate of 18,000 Btu/hr in a 12-in.-diameter pot, the pot outer wall was cooled from 700 to 475°C in 5 hr, with 50 scfm cooling air per zone (300 scfm total) on the external side of the furnace susceptor. With an additional 50 scfm of air supplied directly to the pot outer wall, the outer wall was cooled to a steady state of 450°C in the same 5-hr period. A maximum steady-state heat-removal rate of approximately 5000 Btu/hr per zone is estimated at a wall temperature of 800°C using 50 scfm cooling air per zone.

The performance of the prototype furnace during the 450 hr of actual pot-calcination use was exceptionally good.[24] Each zone of the prototype furnace can be controlled within ±20°C of the set point without gross influence from adjacent zones.[24] The prototype furnace uses a temperature-controlled susceptor for transfer of heat to or from the pot calciner. The susceptor design for the prototype system was found to be reliable in operation.

In the ORNL pilot-plant study[2,4] of the pot-calcination process, an induction-heating furnace was tested. Operating experience at ORNL with this furnace was summarized in a recent progress report.[1]

Other Literature

The management of radioactive wastes is treated in a recent textbook by Mawson[29] of Canada. He discusses the sources and nature of radioactive wastes, their treatment, storage, and disposal, and methods of monitoring and control. He also examines some of the political and legal aspects of waste management.

A journal article (Ref. 30) describes the storage facilities for high-level-activity wastes and the treatment of all wastes from the processing operations at the Eurochemic processing plant at Mol. At this plant discharged fuel elements from European reactors will be processed for the recovery of fissionable materials. The possibility exists that these wastes will receive only partial treatment and will then be transferred to the adjacent Centre d'Études l'Énergie Nucléaire (CEN) site for treatment in the CEN waste-treatment plant.

An economic study of the CEN waste-treatment plant has been published.[31] Information on methods of waste treatment, storage of concentrated wastes, and ultimate disposal of treated wastes is presented. Data on activities and monthly running expenses are tabulated.

A description of an incinerator installation for radioactive wastes is presented in a journal article by French workers at the Marcoule Center.[32] Efficiency of the off-gas purification system and operation of the installation are discussed. Data on operating costs are also given.

The English translation[33] of a Japanese paper on the operation of waste-treatment equipment at the Japan Atomic Energy Research Institute is available. Performance data obtained in tests with nonradioactive and radioactive (actual) wastes are presented for the following equipment systems: flocculation and ion exchange, evaporator, and incinerator. The test results showed that all equipment systems performed satisfactorily and fulfilled their design objectives.

Clark, Godbee, and Fitzgerald[34] at ORNL have summarized the results of previously presented laboratory work[35] investigating the conversion of Purex-plant wastes to glassy solids. Two fixation procedures are being developed, a rising level (RL)-potglass process and a continuous (CON)-potglass process. The following are some of the results of this investigation:

1. For sulfate-containing Purex wastes, phosphate, alumina, sodium, lithium, and calcium were shown to be suitable fluxing additives. Ninety-five percent or more of the sulfate was retained in the glassy product. For nonsulfate-containing Purex wastes, phosphate and lead were found to be suitable fluxing agents. The minimum volume of satisfactory glassy product formed corresponded to about 2.7 gal of solid per ton of uranium processed.

2. Sulfate and nonsulfate Purex wastes containing fission products were converted to glassy solids. In the presence of fission products, both

the melting temperatures and the viscosities of the resultant melts usually increased. The addition of extra fluxing additives was required in order to maintain low melting temperatures and fluidities.

3. Stainless steel was a satisfactory construction material for the fixation pot-storage container in the RL-potglass process. Titanium was found to be a very satisfactory construction material for the continuous evaporator, the condenser, and the off-gas system, which are common to the two processes.

4. Methods were available for lowering the volatility of ruthenium and cesium to approximately entrainment quantities and for removing mercury[36] from wastes.

Deep, permeable geologic formations are being studied for the possible storage of large volumes of fuel-processing-plant low-level-activity wastes that have received some preliminary treatment. Information in a report[37] that describes the subsurface geology and hydrology for six basin provinces in the United States enables preliminary evaluation of their use in the storage of these wastes. The basins studied include Appalachian, Valley-and-Ridge, Michigan, Salina, Denver, and San Juan.

In the period April 1961 to August 1964, 2 megacuries of ^{137}Cs was recovered from Hanford wastes (Purex supernatant 103A, a basic 9*M* $NaNO_3$ solution) and shipped to ORNL for cesium source fabrication.[38] Prior to shipment the cesium is selectively adsorbed on an aluminosilicate ion exchanger, Decalso, contained in a shielded tank. The shielded tanks, after sealing, are shipped via rail from Hanford to ORNL. Hanford is now carrying out an investigation[14] to increase the ^{137}Cs loadings in shipping containers. Synthetic zeolites, such as Linde AW-500, are being considered for adsorption of the cesium in place of the Decalso now being employed. Recent laboratory data indicate that a threefold increase in cesium loadings may be expected with Linde AW-500; the quantity of ^{137}Cs shipped in a shielded tank would increase from 50 kilocuries to 150 kilocuries.

(P. Fineman)

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Section

V

Reactor Fuel Processing

Production of Uranium, Thorium, and Plutonium and Their Compounds

Production and Properties of Uranium Oxides

In the production of uranium compounds from raw materials, separation and purification of uranium are frequently achieved by selective precipitation of uranium from solution in the form of uranates. A detailed study of this class of uranium compounds has been reported in a symposium of papers edited by Spitsyn.[1] These papers present data on the solubility, thermal stability, and mechanism of the formation of uranates, as well as data on the physicochemical properties of various uranates.

Conversion of UNH to UO_3

Although the thermal decomposition of uranyl nitrate hexahydrate (UNH) is an established method for the production of UO_3, many uncertainties exist in the process performance owing to the lack of information on the decomposition reaction. In a study of the decomposition of uranyl nitrates in the presence of steam, Lodding and Ojamaa[2] observed that the predominant gaseous reaction products during nitrate decomposition are H_2O and HNO_3. The thermal decomposition of UNH in dry air proceeds in four steps: at 110°C four molecules of water are given off, and the dihydrate is produced; at 175°C an additional water molecule is evolved; between 210 and 220°C the anhydrous nitrate salt is produced; and at 250 to 270°C the final decomposition to UO_3 occurs. In a steam atmosphere the decomposition of UNH proceeds by a slightly different path: at 110°C four molecules of water are evolved, and the dihydrate is produced; at 180°C the two remaining H_2O molecules are lost, and the anhydrous salt is produced; at temperatures between 180 and 200°C, anhydrous uranyl nitrate decomposes with the formation of $UO_3 \cdot 0.8H_2O$; and at 260°C the final dehydration to UO_3 occurs.

It was observed,[2] from analysis of the effluent condensate, that over 91% of the nitrate in UNH was recovered as nitric acid when the decomposition was conducted in a steam atmosphere. Essentially no nitric acid was recovered in the condensate in tests in which the decomposition was carried out in dry air.

Reduction of Uranium Oxides

Gas–solid reactions, particularly the reduction of uranium trioxide with hydrogen and the hydrofluorination of uranium dioxide to produce uranium tetrafluoride, are important steps in the production of both uranium metal and uranium hexafluoride. The rate of these reactions is determined by the structure of the solid surface which, in turn, is modified by the progress of the reactions. Since the U–O system is highly complex, with the existence of at least five stable oxides reported, the mechanisms governing reduction processes are not readily defined in this system. Heiskala[3] has studied the kinetics of the reduction of UO_3 by hydrogen in the temperature range 575 to 750°C. After an initial period during which the reduction rate reached the maximum value, the reaction proceeded at a constant rate that was independent of the thickness of the reduced UO_2 layer formed on the surface of the particles. The rate-limiting step in the reduction was the reaction at the UO_3–UO_2 interface. Examination of partly reduced samples failed to reveal the presence of any oxides intermediate between UO_3 and UO_2 at the reaction interface.

An activation energy for the reaction was calculated to be 33.3 kcal/mole.

The mechanism of the reduction of beta uranium dioxide (U_4O_9) by acetylene black in the temperature range 700 to 950°C was reported by Vlasov and Tkachenko.[4] On the basis of X-ray analysis, the reduction of U_4O_9 by carbon proceeds with the following phase transformations:

$$U_4O_9 \rightarrow UO_{2+x\,max.} \rightarrow UO_{2+x}$$

The apparent activation energy of the process was calculated to be 55 ± 4 kcal/mole and was practically independent of the degree of removal of oxygen from the oxide. The limiting stage in the reduction reaction was the gasification of carbon by carbon dioxide.

Production of Uranium Dioxide

PROCESSING IN LIMITED GEOMETRY

An evaluation of methods for carrying out gas–solid reactions in equipment that is nuclearly safe by shape and size was made by Taylor and Dell.[5,6] The study concerned the hydrogen reduction of UO_3 particles (produced by fluid-bed denitration of UNH) to UO_2 and the hydrofluorination of the UO_2 to UF_4. On the basis of critical review of process equipment, a horizontal screw-flight stirred-bed reactor was most suitable for conducting the gas–solid reactions. The stirred-bed reactor was operated with countercurrent solids and gas flows. Uranium trioxide was reduced to UO_2 at rates up to 3 kg/hr in a 2-in.-diameter stirred-bed reactor.[5] The reactor incorporated a system of heaters that could provide a reaction–temperature profile along the length of the reactor. When the reactor was operated as a differential contactor, an apparent activation energy for the reduction reaction of 29 ± 2 kcal/mole was obtained. This value indicates the absence of diffusional resistance in the bulk gas phase, a situation that was confirmed by the negligible influence of stirrer agitation or gas motion on the reaction rate. The absence of diffusional resistance in the gas phase indicates that contacting between solids and gas in the stirred-bed system is excellent.

In tests performed with UO_3 feed activated by hydration, conversions to 99% UO_2 were made at 530°C in pure hydrogen with residence times as short as 12 min. The product UO_2 was a powder that was highly reactive towards hydrofluorination.

Uranium dioxide was hydrofluorinated[6] in the 2-in.-diameter stirred-bed reactor at a temperature of 450°C at rates up to 1.5 kg/hr; products containing 0.01 wt.% UO_2 were obtained. Suitable adjustment of the temperature profile, especially near the solids-inlet end of the reactor, made it possible to reduce the stoichiometric excess of HF to 0.5% and still produce a UF_4 material containing no more than 0.01% UO_2. The apparent activation energy calculated from experimental data obtained from tests on the stirred-bed reactor was 9.5 kcal/mole. The results of these tests[5,6] indicate that, by virtue of the solids and gas transport characteristics and temperature profiles achieved in the stirred-bed reactor, this type of contactor appears well suited to continuous processes for the reaction of solids where extended or well-defined residence times are required and where high levels of conversion are desired in either the solid or the gas phase.

PRECIPITATION FROM CARBONATE SOLUTIONS

In the processing of uranium ores with alkaline carbonate solutions, a uranyl carbonate solution containing approximately 0.6 g of uranium per liter is obtained. A technique for preparing technical grade UO_2 from U(VI) carbonate solutions has been described by Bunji and associates.[7] The method is based on the catalytic reduction of U(VI) with hydrogen. The reaction is carried out at 150°C with 15 atm of hydrogen pressure and a UO_2 catalyst that contains a relative geometric initial surface area of 150 cm^2 per liter of solution. The rate of reaction with UO_2 as a catalyst was proportional to the square root of the hydrogen partial pressure. An activation energy of 10.2 kcal/mole for the reduction reaction was calculated from reaction-rate data obtained in the temperature interval 110 to 150°C. The rate of reaction was directly proportional to the catalyst surface area. The deposition of product UO_2 at the catalyst surface did not appear to affect the properties of the catalyst; the UO_2 product apparently also functions as a catalyst in the reduction.

Since the reduction of U(VI) to U(IV) by the use of UO_2 catalyst is a first-order reaction, it is possible to express the processing time for

the reaction in terms of the time required to reduce one-half of the U(VI) present in solution. In plant-scale tests with a feed solution containing 0.6 g of uranium per liter, 20 g of Na_2CO_3 per liter, and 10 g of $NaHCO_3$ per liter, a "half-time" of 15 min has been routinely attained. The UO_2 product[7] contains about 72 to 75% uranium with the major impurities being 2.3% SiO_2, 1.1% ZrO_2, 2% Na_2O, and 1.5% CaO. If a series of reaction vessels is used, it is possible to produce a waste stream containing 0.003 to 0.005 g of uranium per liter which can be recycled for ore leaching.

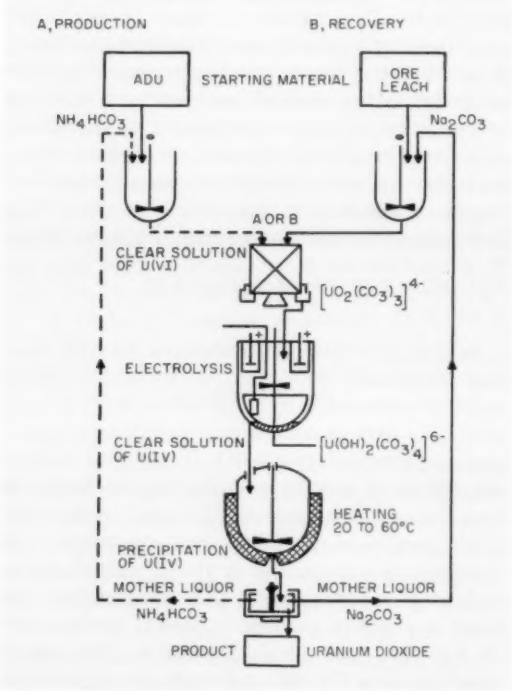

Fig. V-1 The flow sheet for the cyclic process of electrochemical reduction and precipitation. A, production of uranium dioxide from ammonium carbonate solutions; B, recovery of uranium from sodium carbonate ore-leach solutions.[6]

Pravdić, Branica, and Pučar[8] have reported the results of studies on the electrochemical reduction of U(VI) in carbonate solutions to U(IV), as a means for producing uranium dioxide suitable for use as a reactor fuel material. The process involves two steps (see Fig. V-1): (1) the reduction of U(VI) at a mercury cathode to produce a clear stable solution of U(IV) carbonate complexes, and (2) precipitation of hydrated uranium dioxide by heating the U(IV) carbonate solution to 60°C. The process has been applied both to the recovery of UO_2 from uranium ore carbonate leach solutions and to the production of UO_2 from purified solutions of ammonium diuranate (ADU).

REDUCTION OF URANYL HALIDES IN FUSED SALTS

A process for the preparation of coarse crystalline uranium dioxide by the electroreduction of uranyl chloride or uranyl fluoride dissolved in fused chloride salts (LiCl–KCl eutectic) has been described by Schlechter et al.[9] The uranyl compounds are prepared in the melt by the reaction of UO_2 or UF_4 at 500°C with a gaseous mixture of hydrogen chloride and oxygen. Oxides with a composition ranging from $UO_{2.000}$ to $UO_{2.007}$ were prepared by electrolysis in a LiCl–KCl bath at 500°C with a potential between carbon electrodes from 1.00 to 2.00 volts. The crystalline form of the UO_2 product was markedly affected by the presence of moisture in the molten salt, and in the case of the LiCl–KCl–UO_2F_2 system, by the presence of chlorine in the melt. The chlorine tended to induce the formation of oblong crystals. The presence of fluorides in the molten-salt media apparently leads to the preferential formation of cubic UO_2 crystals. Demonstration tests of this process have consistently resulted in the formation of UO_2 crystals with densities between 10.85 and 10.98 g/cm^3.

The results of a pilot-plant study for the preparation of kilogram quantities of UO_2 by electrolysis of uranyl halides in fused KCl–NaCl was published by Hamabe and Ito.[10] In preparation for the pilot-plant tests, a comprehensive investigation was undertaken into the properties of the fused-salt system. As a guide for the selection of the fused-salt solvent, data were obtained on the activity of the oxygen ion (O^{2-}) in the uranium system, and it was observed that fused-salt systems which were accepters of the O^{2-} ion were satisfactory for the production of sound UO_2 crystals. For UO_3 or wet uranyl halide, HCl was a suitable accepter of the O^{2-} ion.

High-density UO_2 was prepared in the pilot-plant tests[10] by reduction of UO_2F_2 or $UO_2Cl_2 \cdot 2H_2O$ in the KCl–NaCl eutectic at 750 to 850°C

with current densities between 2 and 50 ma/cm^2. The crystalline UO_2 particles had densities up to 10.75 g/cm^3 and total impurities of less than 0.1 wt.%.

Sintering of Uranium Dioxide

Most water-cooled water-moderated nuclear power reactors utilize sintered uranium dioxide as the fuel. This fuel must be of high density (93% of theoretical density) to assure dimensional stability of the fuel and a high degree of fission-gas retention. Uranium dioxide powders are produced by several different methods, and the sintering properties of the powders are determined by the method of preparation.

Imris[11,12] has investigated the effect of methods used to produce U_3O_8 on the sintering properties of the UO_2 powder prepared by hydrogen reduction of U_3O_8. The U_3O_8 used in these tests was derived from calcination of ADU at temperatures of 600 to 1000°C. On the basis of UO_2 sintering tests, U_3O_8, prepared by calcining ADU at 700°C, produced a UO_2 powder that sintered to the highest density. It is suggested that the most significant property of the UO_2 product in terms of sintering behavior was the crystallite size. It was observed that the U_3O_8 crystallite size increased greatly with an increase in the ADU calcination temperature, and this effect was transmitted to the UO_2 upon reduction of U_3O_8. Several physical and chemical properties of UO_2 powders were studied to determine if a correlation exists between certain characteristics of UO_2 powders and the sintered density of pressed UO_2 pellets.[13]

The effects of compacting pressure and sintering atmosphere on the sintered density of UO_2 bodies have been reported by Ristić, Radić, and Zivanović[14] and by Javanović et al.[15] It was shown that the final sintered density is related to the density of the UO_2 compact before sintering. An improvement in the sintered density was achieved[14] by an increase in the compacting pressures up to 5 tons/cm^2. Organic binders and lubricants are generally added to ceramic UO_2 powders to facilitate pressing prior to sintering. Since these materials are largely volatile and contain no neutron-absorbing elements, they were presumed to be harmless. It now appears that these materials may contribute significantly to irradiation swelling of UO_2 fuel and to the precipitation of uranium metal during exposure to high temperature.[16]

The effects of vacuum sintering on the properties of sintered UO_2 pellets have been reported.[17] In general, it was observed that the main increase in densification and marked grain growth occurred at temperatures 200 to 300°C lower in vacuum than in a hydrogen atmosphere.

Coating of Uranium Dioxide

The encapsulation of uranium dioxide particles within a ceramic or metallic coating provides a fuel material for use at conditions of high temperature and high burnup which may have a significant resistance to corrosion and radiation damage. Workers at Battelle Memorial Institute[18,19] have developed processes for depositing alumina and beryllia coatings on UO_2 particles by chemical-vapor-deposition reactions in a fluidized bed of the particles. Process studies on alumina coating were performed in a 1-in.-diameter fluid-bed reactor with 50 to 100 g of uranium dioxide having an average particle size of 127 to 200 μ. The procedure involved introducing $AlCl_3$ vapor into the hydrogen fluidizing gas stream while H_2O (50% excess) in a helium stream was fed to the reactor through a tube extending axially from the top of the reactor to approximately 0.5 in. below the top of the UO_2 bed. Dense alumina coatings were prepared at bed temperatures of 1000 to 1400°C. At temperatures below 900°C the coatings were highly porous. A two-step coating procedure was devised to minimize contamination of the coating with UO_2 fuel material and to prevent sticking of particles to the reactor walls at high temperatures. Bare fuel particles were first coated with 2 to 5 μ of alumina. The coated particles were leached in nitric acid to remove any UO_2 associated with the coating layer. After drying, the particles were coated with an additional layer of alumina. Coating rates of approximately 4.5 μ/hr with 50% utilization of the aluminum chloride feed were generally achieved.

Beryllia coatings of high purity were applied[19] to UO_2 particles at temperatures from 500 to 1500°C. The equipment used in coating tests at temperatures above 1200°C is shown in Fig. V-2. Beryllium chloride was generated in the apparatus by reaction of HCl with beryllium metal at 650°C; this procedure appeared much more satisfactory than vaporization of $BeCl_2$ into the hydrogen gas stream. The coat-

ing efficiency (percentage of beryllium chloride appearing as an oxide coating) varied from about 85% at 1500°C to 40 to 65% at temperatures of 600 to 1100°C.

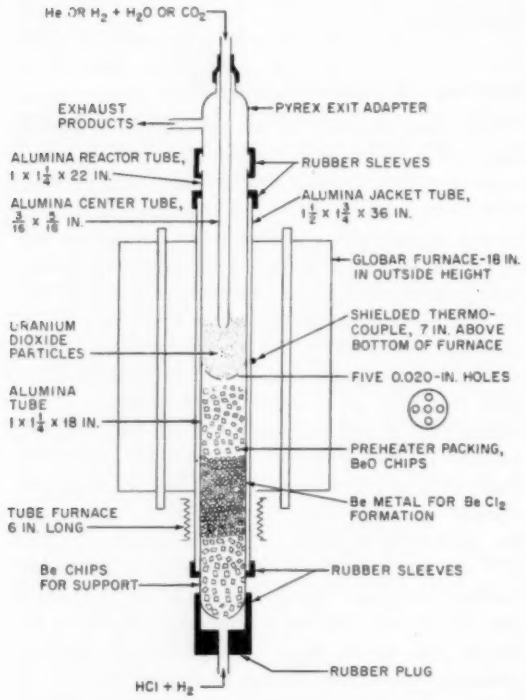
He OR H_2 + H_2O OR CO_2
EXHAUST PRODUCTS
PYREX EXIT ADAPTER
ALUMINA REACTOR TUBE, 1 x 1¼ x 22 IN.
RUBBER SLEEVES
ALUMINA CENTER TUBE, 3/16 x 5/16 IN.
ALUMINA JACKET TUBE, 1½ x 1¾ x 36 IN.
GLOBAR FURNACE-18 IN. IN OUTSIDE HEIGHT
SHIELDED THERMO-COUPLE, 7 IN. ABOVE BOTTOM OF FURNACE
URANIUM DIOXIDE PARTICLES
FIVE 0.020-IN. HOLES
ALUMINA TUBE 1 x 1¼ x 18 IN.
PREHEATER PACKING, BeO CHIPS
Be METAL FOR $BeCl_2$ FORMATION
TUBE FURNACE 6 IN. LONG
Be CHIPS FOR SUPPORT
RUBBER SLEEVES
RUBBER PLUG
HCl + H_2

Fig. V-2 Apparatus constructed of high-purity alumina for preparing BeO coatings.[19]

Workers at Oak Ridge National Laboratory are investigating methods for applying pyrolytic carbon coatings on UO_2 and carbide particles.[20] Coating studies currently involve the deposition of pyrolytic carbon by pyrolysis of methane at 1300 to 2000°C in a fluidized bed. A series of tests was performed at temperatures from 1300 to 2000°C in which the methane flow rate was independently varied relative to the initial surface area of the UO_2 charge while maintaining a constant total gas flow. Contour plots of the crystallite sizes of the coatings showed that the crystallite size increased systematically from 35 to 140 A with increasing temperature and decreasing flow rate. The coating density also increased systematically from 1.5 to 2.1 g/cm^3 with an increase in temperature above 1600°C and a decrease in flow rate.

Production of Uranium Metal

Reduction of Uranium Tetrafluoride

Massive uranium metal is produced at the National Lead Co. of Ohio by a thermite type reaction. In the present plant process, steel reaction vessels lined with magnesium fluoride slag are packed with a loose blend of uranium tetrafluoride and magnesium granules. The vessel is capped and heated in a furnace until reaction occurs. After cooling, the uranium derby that has formed at the bottom of the reaction vessel is separated from the by-product magnesium fluoride slag. Significant economic advantages would be expected to result from modifying the batch reduction process to a continuous process. A pilot-plant facility was constructed to evaluate the feasibility of producing uranium metal by magnesium reduction of UF_4 on a semicontinuous basis.[21]

In this process, briquettes of a blend of UF_4 and magnesium were reduced in an induction-heated graphite reactor to produce uranium metal. The briquettes, which were produced on a rotary press [see *Reactor Fuel Processing*, 6(1): 62-63 (January 1963)], were continually charged into and reduced in the reactor until the reactor was full of molten uranium and MgF_2 slag. The slag was decanted into a mold and the reduction resumed. After three such reduction steps, enough uranium had been produced to warrant tilt-pouring the metal into a mold (see Fig. V-3). The optimum operating temperature was 1340 to 1400°C. Tilt-pouring of the furnace was used since reliable repetitive bottom-tapping methods could not be perfected.

In its final form the reduction unit consisted primarily of an induction-heated graphite reactor, 11.5 in. in inside diameter, 14 in. in outside diameter, and 22 in. high, inside a zirconia housing. The furnace was equipped with a pouring lip on each side. In several tests a spinel (magnesia–alumina) crucible was used to reduce carbon contamination of the uranium resulting from the graphite crucible. However, the aluminum content of the uranium product was then high. Moreover, because of the poor thermal conductivity of the spinel crucible, the metal production rate was much lower than in tests with the graphite reactor. Results of two

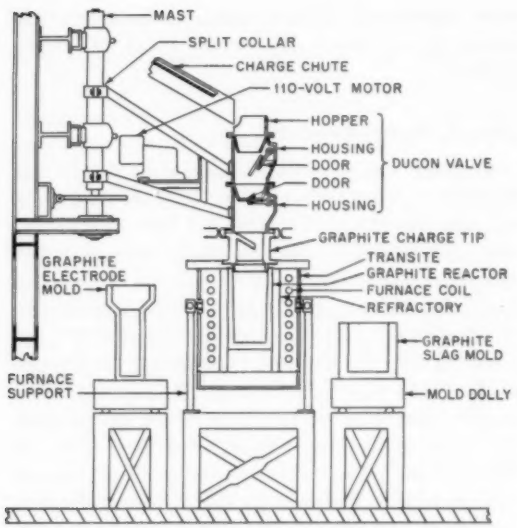

Fig. V-3 Section view of tilt-pour reactor with charging valve.[2]

pilot-scale tests with the graphite reactor are given in Table V-1.

When using UF_4 from reduction of UF_6, the yields of uranium obtained by the semicontinuous reduction process were the same as those obtained by the bomb reduction process. With green-salt feed material containing appreciable amounts of oxygen-containing compounds, ammonium oxalate-insoluble (AOI) and water-soluble content greater than 2 wt.%, the yields of uranium from the semicontinuous process were less than yields achieved by the bomb reduction process. It is expected that the yield of uranium from oxygen-containing UF_4 could be increased slightly by lowering the furnace operating temperature to approximately 1250°C since the reduction of uranium oxides by magnesium would be thermodynamically favored at this temperature. It would be necessary, however, to flux the slag with CaF_2 or NaF in this case to lower the slag melting point below the operating temperature.

Table V-1 RESULTS OF PILOT-SCALE SEMI-CONTINUOUS REDUCTION TESTS* WITH UF_6-SOURCE GREEN SALT[21]

	55-hr test	5-day test
Process conditions†		
Average briquette charge rate, lb/min	35	33
Briquettes used, lb	22,250	46,320
Test results		
No. of reductions made	111	234
No. of derbies made	37	78
Uranium produced, lb	13,926	29,116
Average uranium production rate, lb/hr	253	275
Average derby yield after grit blasting, %	94.5	94.7
On-stream, %	90‡	92§

*The tests were carried out in 11.5-in.-ID by 14-in.-OD by 22-in.-high graphite reactors.

†The reduction and pouring temperatures were 2450 and 2550°F, respectively.

‡First reactor was used for 29 hr, and a second, for 26 hr.

§First reactor was used for 50 hr; a second, for 28 hr; and a third, for 28 hr.

Electrolytic Reduction of Uranium Dioxide

Workers at the Mallinckrodt Chemical Works and at the U. S. Bureau of Mines have developed methods for producing high-quality uranium metal by electrolytic reduction of uranium dioxide in a molten fluoride electrolyte. Descriptions of the processes have been given in previous issues of *Reactor Fuel Processing*.[22–25] Several investigations were performed on the physical properties of the electrolytes to provide a scientific basis for effecting improvements in the design of the electrolytic cells.[26,27] Electrical conductivities and densities of the $LiF-UF_4$, $LiF-ThF_4$, $NaF-UF_4$, and $NaF-ThF_4$ systems were measured[26] at temperatures between 750 and 1000°C. The specific conductance and density of the fused salts varied linearly with temperatures. As the actinide-metal-fluoride concentration was increased from 0 to 60 mole % at 1000°C, the specific conductance of the salt decreased from 9.8 to 2.5 $(ohm\text{-}cm)^{-1}$. In other work Varwig[27] has determined the solubility of UO_2 in several metal-fluoride-salt mixtures at 1150°C. The solubility of UO_2 in fluoride salts increased markedly with an increase in UF_4 concentration in the melt. The solubility of UO_2 varied from 0.1 wt.% UO_2 at 0 wt.% UF_4 to 2.3 wt.% UO_2 at 45 wt.% UF_4.

(J. J. Barghusen)

Production and Properties of Uranium and Plutonium Carbides

Because of the widespread interest in carbide fuels, development work is being carried out at

a number of locations on methods of synthesizing uranium and plutonium carbides and mixed carbides. Since the mechanical and chemical properties of these fuels are greatly affected by carbon content, especially in the region of a carbon-to-metal ratio of 1, emphasis is being placed on precise control of the carbon content of the product.

Carbothermic Reduction Method

Work is being done at United Nuclear Corporation and at The Carborundum Company on the development of the carbothermic reduction method for the preparation of carbides.[28] Fifty-gram reaction mixtures of PuO_2, UO_2, and carbon were blended, cold pressed, and reacted in helium at 1625°C to produce pellets of $(U_{0.95}Pu_{0.05})C_{0.98}$. The carbon content of pulverized reaction products from eight batches varied between 4.66 and 4.94 wt.% (average, 4.79 wt.%) as compared with the intended carbon content of 4.70 wt.%. X-ray diffraction analysis of a composite, prepared by ball-milling a mixture of the products from the eight runs for 24 hr, indicated a cell size, a_0, of 4.959 ± 0.001 A.

The carbothermic technique was also applied to the preparation of $(U_{0.8}Pu_{0.2})_2C_3$ in two experiments.[28] These produced about 4 and 25 g of nearly stoichiometric material by reacting pellets at 1650°C which were prepared by blending and cold-compacting a mixture of PuO_2, UO_2, and carbon in stoichiometric proportions.

Skavdahl[29] has continued studies of the reaction sequence in the carbothermic reduction of PuO_2 to PuC. The reduction under vacuum of PuO_2 to alpha or beta Pu_2O_3 in 1 or 2 hr required a reaction temperature of 1625°C or higher, whereas reduction to PuO, PuC, or Pu_2C_3 occurred in the same time at reaction temperatures of 1400 to 1500°C. A plutonium monooxycarbide phase, Pu(O,C), more volatile than beta Pu_2O_3, is formed during the carbothermic reduction of PuO_2. Appreciable volatilization of Pu(O,C) occurs at 1550°C. The measured melting point of Pu(O,C) containing approximately 0.5 wt.% carbon is 1900°C.

Strasser et al.[28] prepared Pu(O,C) containing only 0.15 wt.% carbon by carbothermic reduction of PuO_2 in helium at 1750°C. In attempts to synthesize carbon-stabilized $(U_{0.8}Pu_{0.2})O$, however, large amounts of a dioxide type phase were obtained as well as a monoxide type phase in a product that contained about 1 wt.% carbon.

Liquid-Metal Process

Various methods of synthesizing UC and (U,Pu)C are under study at Argonne National Laboratory (ANL).[30] Powdered UC with excellent pressing and sintering properties has been produced on a scale of 1 kg per batch by a liquid-metal technique. In this process carbon is added to a zinc–magnesium solution of uranium at 800°C, UC is precipitated, and magnesium and zinc are removed by siphoning and distillation. The oxygen content of the product has been acceptably low (0.20 wt.% or lower in recent runs); the carbon content of the product has ranged between 5.04 and 5.59 wt.% for a carbon-to-uranium ratio in the charge of 1.02.

Molten-Salt Process

Another method investigated at ANL[30] for the synthesis of carbides involved the reaction of UCl_3 and $PuCl_3$ with Mg_2C_3 at 650°C in a molten-salt solvent (LiCl or 35 mole % LiCl–65 mole % $MgCl_2$). Initial experiments showed that reaction of UCl_3 with Mg_2C_3 produced UC; however, $PuCl_3$ reacted to form Pu_2C_3 rather than the desired monocarbide. In experiments with mixtures of UCl_3 and $PuCl_3$, minor amounts of a sesquicarbide phase as well as the monocarbide phase were observed in the products by X-ray diffraction analyses. Moreover, the oxygen and free carbon contents of the products were high, each being generally in excess of 1.0 wt.%. As a result no further investigation of this method of preparing carbides is planned.

Fluid-Bed Process

A fluid-bed technique for preparing UC from the metal is also reported by ANL.[30] In this technique uranium is first hydrided and then contacted with a hydrogen–propane mixture at 500 to 700°C. Both hyperstoichiometric and hypostoichiometric UC were produced by varying the hydrogen-to-propane ratio. Carbon deposition was prevented by selecting the proper hydrogen-to-carbon ratio at the operating temperature. However, at hydrogen-to-carbon ratios that would be expected to yield UC_2, as indicated by data on free-energy changes, the product was found to be mainly UC.

Reaction of Uranium with Graphite

Takeuchi, Honma, and Satow[31] studied reactions of uranium metal with graphite in the temperature range of 800 to 1100°C. Metallic uranium was in contact with graphite for 3 to 50 hr in vacuum, and the amount of carbide formed was determined. The reaction rate was parabolic, and the activation energy for the reaction was found to be 59 kcal/mole. The holding of a tungsten wire between the uranium and the graphite during the reaction to mark the original interface permitted a demonstration that the growth of the carbide film was due mainly to the migration of carbon. From these results the rate-determining step seemed to be the diffusion of carbon through the carbide film on the metal surface. The composition of the film was determined by hydrolysis of the carbide and chromatographic analysis of the hydrocarbon gas formed. The ratio of ethane to methane indicated that, within the accuracy of the technique, the carbide film consisted entirely of the monocarbide. The results were confirmed by X-ray diffraction analyses. The lack of UC_2 in the carbide film indicates that carbon diffuses much more rapidly through UC than through UC_2. The diffusion coefficient of carbon in UC as a function of temperature was calculated from the parabolic rate constants.

Sintering Properties of UC and UN

Good sinterability is a desirable characteristic for any ceramic fuel. High fuel density minimizes fission-gas release and maximizes thermal conductivity. Good sinterability is characteristic of carbide fuel powder that has low oxygen content and fine particle size. Nickel and UAl_2 have been used as additives in sintering UC to obtain high theoretical densities at moderate temperatures as reported previously in *Reactor Fuel Processing*.[32]

Uranium mononitride powder was sintered[33] to 95% of theoretical density by grinding to a very fine powder, die pressing, and sintering in flowing argon at 1700°C. The nitride was prepared by reacting uranium powder with a flowing atmosphere of 50% N–50% Ar at 900°C and decomposing the U_2N_3 to UN at 1400°C under argon flow. The nitride was milled in a tungsten carbide vibratory mill. Resulting particle sizes were 0.1 to 1.0 μ after 8 hr of grinding and 0.05 to 0.5 μ after 128 hr of grinding. Great improvement was noted in the sintered density of the pellets with up to 8 hr of milling, and the optimum milling time was 16 to 30 hr. The compacting pressure was also an important variable. The sintered density increased with increasing pressure up to the maximum pressure employed of 80 tsi. Pellets pressed at 40 tsi from powders milled for 20 hr reached a density of 85.5% of theoretical when sintered for 2 hr at 1450°C and a density of 94.8% of theoretical when sintered for 2 hr at 1700°C. Oxidation of the powder prior to sintering appeared to reduce the sintered density.

(P. A. Nelson)

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Section

VI

Reactor Fuel Processing

Safety in Chemical Processing

Criticality Incidents in Fuel-Processing Plants

Incident at the United Nuclear Corporation Plant

On July 24, 1964, a criticality incident occurred at the U. S. Atomic Energy Commission (AEC)-licensed plant of the United Nuclear Corporation at Wood River Junction, R. I. Descriptions of the operations at the plant, the events surrounding the incident, and the conclusions and recommendations of the review committee appeared in a previous issue of *Reactor Fuel Processing*.[1] The information presented in Ref. 1 was based on a report[2] of a committee formed specifically to investigate the event. A supplemental report dealing with results of investigations on the nuclear and physics aspects of the incident has been issued by the United Nuclear Corporation[3] and is available for public inspection at the AEC Headquarters Public Document Room. The objectives of the investigations included: (1) reconstruction of the initial conditions surrounding the criticality and the nature of the system that went critical, (2) determination of whether criticality continued after the initial excursion or whether a subsequent excursion occurred, (3) estimation of the total number of fissions that occurred, and (4) estimation of the radiation doses received by exposed personnel.

After interpretation of all available data, the following conclusions were reached concerning the incident:

1. The first excursion occurred when a solution of concentrated uranyl nitrate (256 g/liter) was poured by the operator from a container of safe geometry into an 18-in.-diameter vessel of unsafe geometry. Approximately 2600 g of ^{235}U were in the system when criticality first occurred.

2. A second excursion probably occurred when the system still contained approximately 1870 g of ^{235}U. At this time the electric stirrer was turned off when the superintendent and supervisor were draining the contents of the tank into a safe-geometry container.

3. Total fissions that occurred are estimated to be $1.3 \pm 0.25 \times 10^{17}$: 1.0×10^{17} to 1.1×10^{17} fissions from the first excursion and 0.2×10^{17} to 0.3×10^{17} fissions from the second.

4. Radiation doses received by personnel were estimated to be as follows: operator, 10,500 rads (lethal); superintendent, 60 to 91 rems; supervisor, 64 to 104 rems.

A description of the clinical history of the operator has been published by Karas and Stanbury.[4] Although the medical aspects of the accident are beyond the scope of this review, the concern of the authors with the radiation-safety and administrative procedures required in the management of a victim of a nuclear accident is pertinent. Immediate on-site care of the exposed person imposes a formidable exercise in radiation safety. In this instance the patient had heavy surface contamination of radiation-emitting isotopes. Furthermore, vomitus, sweat, urine, and feces were all contaminated with radioactive ^{24}Na and ^{32}P. Thus there was the problem of radioexposure to the personnel caring for the patient, as well as the disposal of contaminated clothing and radioactive excreta, especially since the patient was immediately incontinent.

Karas and Stanbury[4] stress the importance of establishing a tight medical and administrative control at the earliest possible moment. The management of the patient, the legal implications, the possibility of serious contamination, and the enormous local interest generated by

the accident impose especially difficult administrative problems. The authors also highly recommend that matters of radiation safety should be entirely in charge of the hospital radiation-safety officer and that every hospital within reach of a nuclear installation should have such a person on its staff.

Accidental Nuclear Excursion in Recuplex Operation at Hanford

An accidental nuclear excursion occurred in the Recuplex facility at Hanford Atomic Products Operation on Apr. 7, 1962. The Recuplex facility is a multipurpose plutonium operation in which plutonium is recovered and purified from a variety of waste streams primarily originating in the Plutonium Processing Plant at Hanford. Plutonium recovery and purification is accomplished by solvent extraction from an impure nitric acid solution with the use of a solvent of 20% tributyl phosphate in carbon tetrachloride. The entire facility was located in a large hood designed specifically for plutonium service.

The nuclear excursion occurred in a general-purpose transfer tank of unfavorable geometry as the result of an inadvertent transfer to the tank of 45 to 50 liters of dilute nitric acid containing approximately 1400 to 1500 g of plutonium.[5] The total number of fissions, estimated by analysis of the contents of the tank, was 8×10^{17}. The tank was provided with essentially no shielding to protect operators of the equipment against escaping neutrons or gamma rays. Of the 22 persons in the building at the time of the incident, three were hospitalized for observation and treatment after the accident. These three received estimated whole-body doses of 110, 43, and 19 rems. A summary of the biologic effects observed over a two-year period on these individuals has been recently published.[6] The radiation-protection aspects of the Recuplex incident have also been published in a report.[7]

The investigating committee that reviewed the Recuplex incident[5] commended the prompt, competent, and considered manner in which the emergency was handled. The committee also formulated several recommendations[5] that can be applied to similar facilities in which fissionable materials are being processed:

1. Facilities of this type should provide personnel protective shielding, at least around geometrically unfavorable vessels, and should make generous use of nuclear poisons, of remote-control techniques, and of automatic, continuous, visible recording of process parameters important to nuclear safety.

2. Wherever feasible, equipment should be of geometrically favorable design. Where plutonium containing ^{240}Pu is being handled, neutron counters should be installed on key equipment. Such neutron counters should be arranged so as to give an automatic alarm if the counting rate exceeds a set maximum, depending on the ^{240}Pu content.

3. Operating procedures should ensure that all possible modes of operation are recognized, and operating personnel should be trained to understand and apply these procedures.

4. As-built drawings should be kept current, and procedures should be promptly modified to take into account changes in equipment, piping, and instrumentation.

5. Close operating controls should be exercised through the use of log books, frequent sampling and analysis of vessel contents, close control of plutonium inventory, and checking of the status of the facility at shift changes. Each operator coming on shift should recognize his responsibility for verifying the condition of the equipment as told to him by his predecessor on the previous shift.

6. A facility subject to a wide variety of feed materials and consequently to variation in operating conditions should be given an unusual degree of technical surveillance, particularly during nonroutine operations.

Compatibility Studies with Anion-Exchange Resins

In two previous issues of *Reactor Fuel Processing*,[8,9] details were reported of two incidents, each involving a fire and the pressurization of an anion-exchange contactor used in the purification of plutonium from nitric acid solutions. The significance of these events was the realization that the maximum safe operating temperature for plutonium anion-exchange systems is substantially lower than previously thought and that nitrate-loaded anion-exchange resins are capable of undergoing decomposition with the evolution of gases under a variety of conditions.

As the result of an incident at the AEC Rocky Flats plant[9] in 1963, a series of laboratory

tests was made to determine the compatibility of anion-exchange resins with nitric acid and the ignition properties of resins admixed with several materials.[10] Samples of Dowex 1-X4 anion-exchange resin were contacted with 7*N* and 12*N* nitric acid at 50 and 100°C for periods up to 14 days. The quantity of resin that was extracted into the nitric acid varied widely. The extract solution, when evaporated to dryness, yielded a material that was insoluble in CCl_4 but soluble in water. The dried resin extract was used in an investigation of the ignition properties of resin materials. In the ignition tests, resin that had been previously treated with nitric acid was mixed with dried resin extract and dried extracts prepared by leaching Mayon, Tygon, and thermoplastic tubing with 7*N* or 12*N* HNO_3 at 50 to 100°C. The mixtures were found to react exothermally at temperatures as low as 110°C. Some mixtures ignited spontaneously at temperatures as low as 135°C. In several tests the gaseous decomposition products burned or exploded when ignited by a spark gun.

It was observed in these tests that hot nitric acid will leach both chloride and plasticizer from plastic tubing. Of several varieties of tubing evaluated, Tygon tubing appeared most resistant to degradation by nitric acid.

In an effort to simulate the conditions that were believed to have existed at the time of the incident,[9] an ion-exchange column containing Dowex 1-X4 resin was loaded with plutonium and allowed to remain in an unvented condition. Although a pressure buildup was noted, no significant temperature increase was observed.[10]

On the basis of the results of the laboratory studies, the following recommendations have been suggested[10] for plutonium anion-exchange facilities:

1. All anion-exchange columns should be vented when not in operation.

2. Tygon tubing should be employed in preference to other varieties of plastic tubing.

3. The resin in anion-exchange columns should never be allowed to become dry.

4. Since a low ignition point has been observed with resin materials, used and degraded resin should be considered a flammable material. Precaution should be taken to prevent spontaneous ignition from external heat sources.

5. Incineration of all used resin appears preferable to disposal by burial.

(J. J. Barghusen and A. A. Jonke)

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